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Rockwell International, Canoga Park, CA. Energy Systems Group

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BROMINATION PROCESS FOR DISPOSAL OF SPILLED HAZARDOUS MATERIALS

by

A. J. Darnell
Energy Systems Group
Rockwell International
Canoga Park, California 91304

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Project Officer

John E. Brugger
Oil and Hazardous Materials Spills Branch
Municpal Environmental Research Laboratory
Edison, New Jersey 08837

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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16. ABSTRACT
A novel process was tested for oxidizing organic materials, and wastes including the so-called "refractories" and pesticides. Bromine and water reacted with such materials at 250 to 300°C to chiefly form CO_2 and aqueous HBr. The HBr solution was electrolyzed at ambient conditions, in a membraneless cell, to produce hydrogen and to regenerate bromine for recycling.

The bromination process was evaluated on both a laboratory and a pilot-plant scale. A simulated spill mixture consisting of malathion, soil, sand, humus, and moisture was successfully treated in an 8-liter, tantalum-lined autoclave at 300°C. Complete destruction of the malathion (>99.9999%) was achieved.

The HBr solution was electrolyzed in an inclined membraneless cell with graphite electrodes to yield a solution containing about 20 wt% HBr and 18 wt% dissolved bromine. The coulombic efficiency was about 96%.

A conceptual design for a larger-scale batch system was developed. Such a unit could process hazardous wastes at a rate of 7.5 kg/hr. The total cost for such a system installed at an available site was estimated at $625,000 in January 1979. Of this total, $350,000 represented equipment costs.

Laboratory oxidations of γ-lindane and heptachlor were less efficient than when trichloroethane was the substrate, with HBr yields of only 56% and 71% respectively, at 300°, but reaction conditions were not optimized.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American People. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

A variety of processes must be available to the technical community for use in completing the cleanup of spills, and, in general, for the destruction of any hazardous wastes for which other safe alternatives do not exist. This report documents the development of one such technique suitable for halogenated wastes and its evaluation from laboratory experiments to pilot-plant trials.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

ABSTRACT

Rockwell International has conducted process development studies on a novel process for the oxidation of organic materials with concurrent production of hydrogen. In the Rockwell Bromination Process, the material is reacted with bromine and water at 250° to 300°C to form CO_2 and aqueous HBr. The hydrobromic acid solution is electrolyzed, producing hydrogen and regenerating the bromine so that it can be recycled for further use. The hydrogen represents a valuable byproduct which can be marketed or burned to provide heat for the process.

A program was conducted to test the application of the Rockwell bromination process to the disposal of spilled hazardous waste. The overall program consisted of two tasks. Task I involved a laboratory investigation of the bromination reaction with three typical hazardous chemicals and of the regeneration of the bromine reactant by the electrolysis of aqueous hydrobromic acid. Task II consisted of the design, development, testing, and evaluation of a pilot system for the disposal of a simulated spilled hazardous chemical with the recovery of the bromine reactant. The results from Task I were reported in the "Proceedings of the 1978 National Conference on Control of Hazardous Material Spills," (Hazardous Materials Control Research Institute, Silver Spring, MD, 1978. pp. 221-225).

This report describes the results of Task II of the program. Pilot-scale studies of the bromination reaction were conducted using a simulated spill mixture consisting of 70 wt% malathion, 10 wt% soil, 10 wt% sand, 5 wt% humus, and 5 wt% moisture. These tests, scaled up to about 50 g, were performed in a tantalum-lined 8-liter (2-gal) autoclave. They were carried out for 2 hr at 300°C because earlier tests on a smaller scale had shown that agitation could be used to reduce the time for the destruction of the malathion from 5 to 2 hr at 300°C. The extent of the reaction was monitored by measuring the CO_2 pressure. No malathion or other phosphorus-containing organic residuals was detected in the gaseous or liquid products. Based on the sensitivity of the analytical methods used, the extent of destruction of the malathion was $\geq$99.9999%.

The resulting aqueous HBr solution was treated in a pilot-scale electrolysis cell to regenerate the bromine. An inclined membraneless electrolysis cell with graphite electrodes of approximately 100 cm^2 surface area and with an interelectrode separation of 0.61 cm was used for these tests. It was found that deposition of 5.5 mg of platinum per cm^2 on the cathode surface reduced the voltage required for the electrolysis of HBr by about one-half. The 38 wt% aqueous HBr solution obtained from the pilot-scale bromination tests with the malathion-debris mixture was pumped through the electrolysis cell at a flow rate of about 2 ml/min.

Electrolysis was carried out at room temperature and atmospheric pressure. A voltage of 1.25 V was found to be required at an electrode current density of 100 mA/cm^2. The solution exiting from the cell contained approximately 20 wt% HBr and 18 wt% dissolved Br_2. The coulombic efficiency for the electrolysis was 97+1%.

At the suggestion of the EPA Project Officer, laboratory-scale bromination tests were also conducted with the chlorinated hydrocarbons lindane and heptachlor, but the reaction conditions were not optimized.

Conceptual engineering studies were carried out on a bromination system for the disposal of spilled hazardous chemicals. These studies were based on the use of a batch bromination reactor with a capacity of about 22.7 kg (50 lb) of hazardous chemicals. Operation was assumed at 300°C and 8500 kPa (1200 psi) with a turnaround time of 1 hr for an average processing rate of 7.5 kg/hr of hazardous chemical. The aqueous HBr solution from the bromination reactor is then sent to a continuously operated electrolysis cell for regeneration of the bromine. The electrolysis cell was assumed to operate at ambient temperature and atmospheric pressure at an electrode current density of 100 mA/cm^2. Preliminary estimates indicated that the cost of the equipment for such a disposal system would be about $350,000. The estimated total capital cost, including installation at an available site, was $625,000 in January, 1979.

This report was submitted in fulfillment of Contract No. 68-03-2493 by Rockwell International under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period January 1, 1978 to June 1, 1981, and work was completed as of December 10, 1981.

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SECTION 1

INTRODUCTION

The disposal of spilled hazardous substances and wastes requires a considerably higher level of technology than does the disposal of most other wastes. This is due primarily to the potential health and safety dangers involved in handling and detoxifying hazardous materials. The problem is further complicated by the fact that, in a spill situation, the hazardous component may be mixed with solid debris and water. Thus, methods used to dispose of the hazardous waste must be effective in the presence of various nonhazardous materials such as sand, soil, humus, and water.

The generation of hazardous waste in the United States, by both the public and private sectors, is widely distributed geographically. Industry produces the majority of hazardous wastes and the amounts of these wastes are generally in proportion to population density.

This program addresses one approach to the ultimate disposal of spilled hazardous substances including cases where the spilled hazardous material is collected along with accompanying debris.

Rockwell International has conducted development studies on a novel process, based on a bromine oxidation method for the destruction of spilled hazardous chemicals. In the Rockwell bromination process, the spilled hazardous substance is reacted with bromine and water at 250-300°C to chiefly form CO_2 and aqueous HBr. The hydrobromic acid solution is electrolyzed, producing hydrogen and regenerating the bromine so that it can be recycled for further use. The hydrogen represents a valuable by-product, which can be marketed or burned to provide heat for the process. A program was conducted to test the application of the Rockwell bromination process to the disposal of spilled hazardous wastes. The overall program consisted of two tasks. Task I, completed earlier, involved a laboratory investigation of the bromination reaction with three typical hazardous chemicals and of the regeneration of the bromine by the electrolysis of aqueous hydrobromic acid.[1]* Task II consisted of the design, development, testing, and evaluation of a pilot system for the disposal of the waste from a representative hazardous chemical spill with the recovery of the bromine reactant. Intermediate scaled-up testing, approximately ten-fold in size over the Task I tests, was also performed during the time the pilot scale unit was being designed and constructed.

*Numbers refer to citations in the list of references

A conceptual engineering design of a 7.5-kg/h disposal system for spilled hazardous materials, including an estimate of equipment costs, was prepared.

This report covers Task II of the program.

SECTION 2

CONCLUSIONS

The results of the pilot-scale studies showed that the destruction of a hazardous substance such as malathion in a simulated spills mixture consisting of sand, soil, humus, and moisture is essentially complete, i.e., $\geq$ 99.9999%, after reaction for 2 hr at 300°C in an autoclave.

Bromine and/or hydrobromic acid react to a limited extent with sand and soil to form nonvolatile metallic bromides, which would represent a loss of bromine. These bromine losses can be reduced to insignificant amounts (i.e., $\leq$0.01%) by treatment of the metal bromides with sulfuric acid to regenerate Br_2.

The concentrated aqueous hydrobromic acid effluent from the bromine-mediated oxidation reaction of the simulated spills mixture can be electrolyzed to regenerate the bromine. This was performed in a pilot-scale hydrobromic acid electrolysis cell operating at ambient temperature and atmospheric pressure. The concentrated HBr solution is electrochemically reduced to Br_2 in a single pass through the unit to yield a bromine-enriched solution for reuse in the reactor. Relatively small amounts of platinum catalyst (5 mg of Pt per cm^2 of cathode surface) reduce the electrical power required for electrolysis by one-half at practical electrode current densities of 100 mA/cm^2.

The conceptual design of a 7.5-kg/h hazardous chemical disposal-bromine recovery system was carried out. From these studies, it was estimated that the installed cost at an available site would be about $625,000 (January, 1979).

SECTION 3

RECOMMENDATIONS

The results from this study are encouraging. Laboratory tests conducted under Task I show that the bromination process is effective in the destruction of hazardous chemicals such as copper acetate, trichloroethane, and malathion. Pilot-scale testing shows the process is effective in the destruction of a simulated hazardous spill mixture consisting of malathion mixed with debris. The bromine was regenerated at practical current densities and voltages in an electrochemical cell in which small amounts of platinum catalysts had been electrodeposited on the cathode. Bromine losses are small, i.e., less than 0.01% of the bromine used per cycle.

The following recommendations are made:

1) The bromination process should be considered as an option for the destruction of hazardous substances and wastes.

2) Further studies should be carried out to search for catalysts to speed up the oxidative (bromination) reaction rate in order to reduce the reaction time and/or temperature.

3) Work should be undertaken to increase the reactivity of bromine toward chlorinated aromatic hydrocarbons such as lindane and heptachlor. Specifically, catalysts dispersed on ceramic substrates, such as those used in the petroleum industry, should be investigated as a means of increasing the effectiveness of the degradation reaction.

4) Small amounts of platinum deposited on the cathode were effective in reducing the electrical power required for the electrolysis of aqueous HBr. The amount of platinum required should be better defined to make more effective use of the platinum catalyst. Activation of graphite with a nitric acid wash has also been reported to catalyze the electrolysis reaction of aqueous halides on graphite electrodes, This avenue should be investigated to see whether the use of the platinum catalyst can be eliminated.

5) Additional exploratory research is necessary in a number of areas. The mass balance for bromine should be determined as a possible means of improving the overall efficiency of the reactions and as a basis for calculations of operating costs. Intermediates and byproducts should be identified to insure that no new toxic

substances are generated that could be released as "inert" solids, vented gases, or liquid effluents. A screening program should be initiated to cover a broader range of hazardous compounds and better establish the utility of the process.

6) A disposal unit with a capacity of 8 to 10 kg/hr should be constructed for the disposal of spilled hazardous wastes.

SECTION 4

CONCEPT

Disposal of a hazardous carbonaceous spilled chemical is accomplished in this process by degradative reaction with bromine and water at elevated temperature to form aqueous hydrobromic acid (HBr) and carbon dioxide (CO_2).

The reaction of the combustible carbonaceous material, represented empirically by CH, is as follows:

$$CH + 5/2\ Br_2 + 2H_2O \longrightarrow 5HBr\ (\text{aqueous solution}) + CO_2.$$

The CO_2 is stripped of Br_2 and HBr vapors, and released to the atmosphere. The concentrated aqueous HBr solution is processed by electrolysis to regenerate the bromine and form product hydrogen:

$$5HBr\ (\text{concentrated aqueous solution}) \xrightarrow{\text{electrolysis}} 5/2\ H_2 + 5/2\ Br_2\ (\text{in dilute HBr solution}).$$

The bromine, dissolved in dilute aqueous HBr solution, is returned for further reaction with the carbonaceous waste material. The H_2 is stripped of Br_2 and HBr vapors so that it can be used, marketed, or disposed of by flaring. The net overall reaction for the disposal of the oxidizable spilled hazardous material is:

$$CH + 2H_2O \longrightarrow CO_2 + 5/2\ H_2.$$

The process is shown schematically in Figure 1.

The spilled carbonaceous material may contain metal-organic compounds or inorganic materials as part of the accompanying debris. These components will react with bromine and/or hydrobromic acid to form metallic bromides (MBr). Other work carried out at Rockwell International has shown that the metallic bromides can be reacted with concentrated sulfuric acid to regenerate hydrogen bromide, i.e.,

$$2MBr + H_2SO_4 \longrightarrow 2HBr + M_2SO_4.$$

The hydrobromic acid can be distilled off, recovered, and sent to the electrolysis cell for regeneration of the bromine. The metal sulfates can be reclaimed for reuse or discarded at a suitable site.

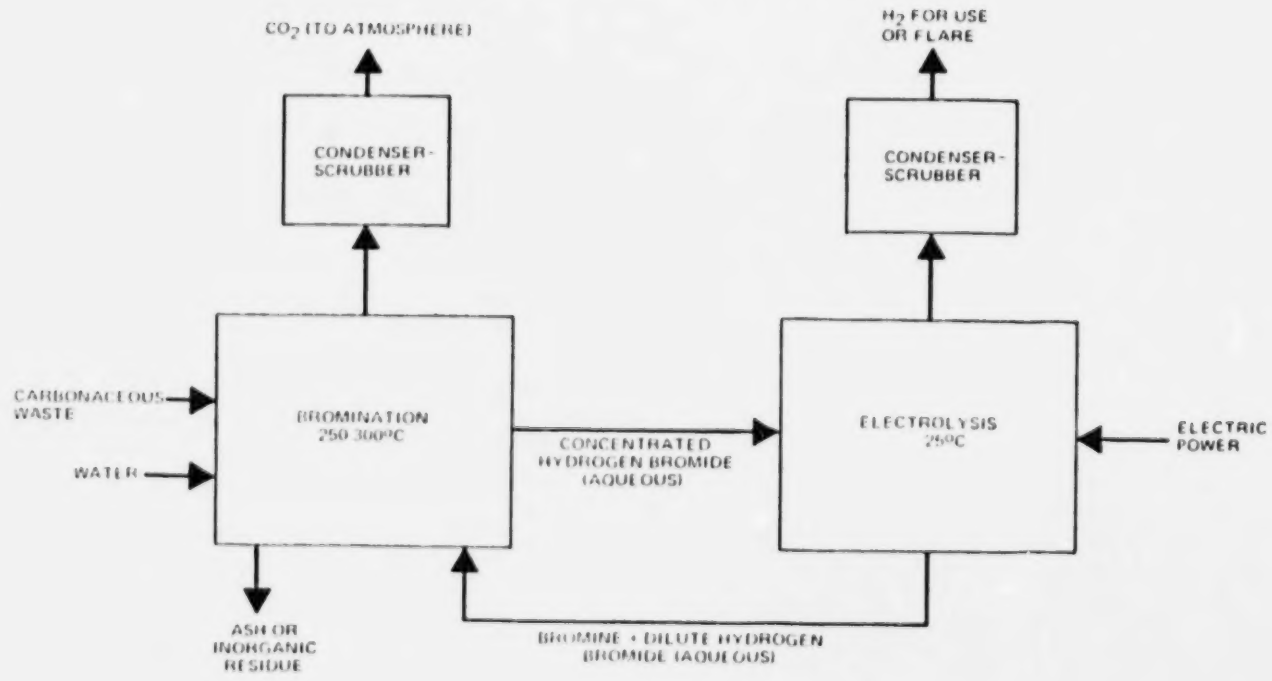


Figure 1. Schematic Flow Diagram for Disposal of Carbonaceous Wastes by the Bromination Process

The key features of the process are: (1) many organic waste materials are oxidized by bromine to CO_2 and a hydrogen halide; (2) a useable product (hydrogen) may be obtained from otherwise useless and hazardous waste; and (3) hazardous metallic compounds can be separated, isolated, and even reclaimed for reuse.

SECTION 5

TASK I RESULTS

BROMINATION

Laboratory-scale investigations with gram amounts of hazardous chemicals were performed in Task I of the program. Bromination reactions were carried out with three typical hazardous materials consisting of a heavy metal organic (copper acetate), a chlorinated hydrocarbon (trichloroethane), and a sulfur-and-phosphorus-containing organic compound (malathion).

The bromination reactions were shown to proceed as follows:

copper acetate: $Cu(C_2H_3O_2)_2 + 4H_2O + 8Br_2 \longrightarrow 4CO_2 + 14HBr + CuBr_2$;

trichloroethane: $CH_3CCl_3 + 4H_2O + 4Br_2 \longrightarrow 2CO_2 + 8HBr + 3HCl$;

malathion: $C_{10}H_{19}O_6PS_2 + 26H_2O + 32Br_2 \longrightarrow 10CO_2 + 64HBr + 2H_2SO_4 + H_3PO_4$.

The preferred conditions of time and temperature, as well as bromine and water stoichiometry, to carry out the bromination reaction were determined using gram-size samples of these test materials. Reaction rate studies at 300°C indicated that destruction of copper acetate, trichloroethane, and malathion were complete in 1, 3, and 5 hrs., respectively. Analyses of the products showed no detectable amount of the hazardous chemical reactants. The sensitivity of the analytical method showed that the destruction of copper acetate was $\geq$99.8%, for trichloroethane it was $\geq$ 99.99%, and for malathion it was $\geq$99.9999%.

Tests were also conducted to show that metallic bromide residues from the reaction of simulated spill mixtures with bromine can be treated with sulfuric acid to lower their bromine content from 240 ppm to 0.6 ppm (for comparison, sea water contains 65 ppm bromine).

ELECTROLYSIS

The published literature on the electrolysis of aqueous HBr solutions was reviewed in Task I of the program. Information on the electrolysis of aqueous HBr was not sufficient to permit establishment of working parameters for the bromine regeneration unit. Work in Task I was concerned primarily with the determination/verification of HBr electrolysis data for development of the process. This work consisted primarily of (a) determination of the thermodynamic or no-load potential for decomposition of aqueous HBr solutions, (b) determination of the decomposition voltage of aqueous HBr

solutions at viable electrode current densities, and (c) determination of the decomposition voltage of HBr solutions at concentrations suitable for the process.(1) A brief summary of the results of these studies follows.

The no-load potential measurements were performed using a four-probe electrode method. Measurements were carried out on the constant boiling mixture (or azeotrope) having a composition of 47 wt% HBr from ambient temperature to 250°C. The data obtained are shown in Figure 2. The data of Glass and Boyle(2) are also shown for comparison. These data show the no-load or minimum voltage required to carry out the electrolysis of a 47 wt% aqueous HBr solution. The no-load decomposition potential drops significantly with increasing temperature, from 0.69 V at 25°C, to 0.34 V at 250°C. However, since the regeneration of bromine for disposal of spilled hazardous chemicals generally involves low throughputs, the engineering complications introduced by operating the electrolysis cell at elevated temperatures and, thus, at elevated pressures, i.e., as high as 5500 kPa (800 psi) at 250°C, outweigh the advantage of the lower voltage and lower power requirement for the high-temperature operation. Thus, it seemed advisable to carry out the HBr electrolysis at ambient temperature and pressure for the disposal of hazardous spilled chemicals.

The voltage required to carry out electrolysis of aqueous HBr solutions at 25°C was measured at electrode current densities ranging from 50 to 400 mA/cm^2. These measurements were performed with HBr solutions covering the concentration range of interest, i.e., from 20 to 65 wt% HBr, using graphite electrodes with 1.0 cm spacing and separated by a 0.10-cm-thick Al_2O_3 fibered-felt membrane. The data from the tests carried out in Task I are shown in Figure 3. From the work of Glass and Boyle(2), it is known that the no-load decomposition potential of aqueous HBr decreases with increasing HBr concentration. However, the data obtained in this study, under load conditions, show that the decomposition voltage of the 65% HBr solution is greater than that of the 47% solution. (The decomposition voltage of the 20% HBr solution is greater than that of the 47% solution, as expected.)

One explanation offered for this observed concentration effect under load conditions, is that there is a maximum in the ionic conductivity of aqueous HBr solutions at a composition of about 45% HBr (as found by Glass and Boyle(2)). Thus, the lower conductivity of the 65% solution as compared with that of the 47% solution brings about a higher IR voltage loss in the 65% solution. This factor could cause the decomposition voltage of the 65% solution, under load conditions, to be greater than that of the 47% solution.

In summary, the electrolysis studies performed in Task I determined: (a) the no-load or minimum voltage required for the electrolyis of a 47wt% HBr solution, (b) the effect of electrode current density upon the decomposition voltage, and (c) the effect of HBr concentration on the decomposition voltage under load conditions. These data were needed to establish suitable conditions for operation of the electrolysis cell.

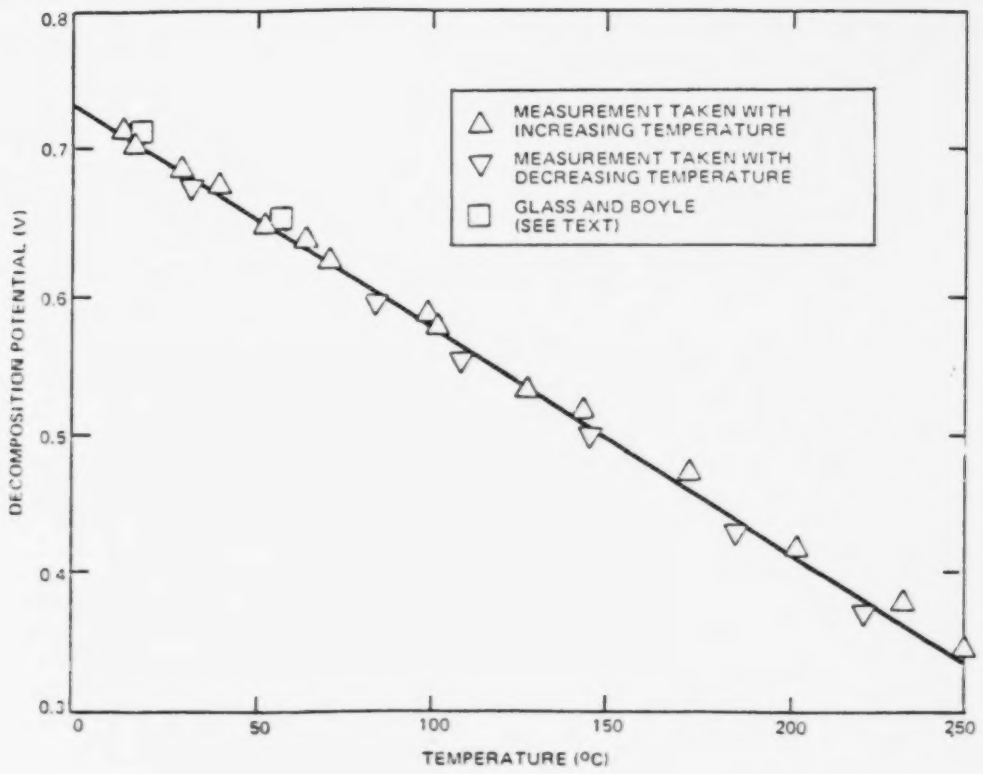


Figure 2. Decomposition Potential of a 47 wt % Aqueous HBr Solution vs Temperature

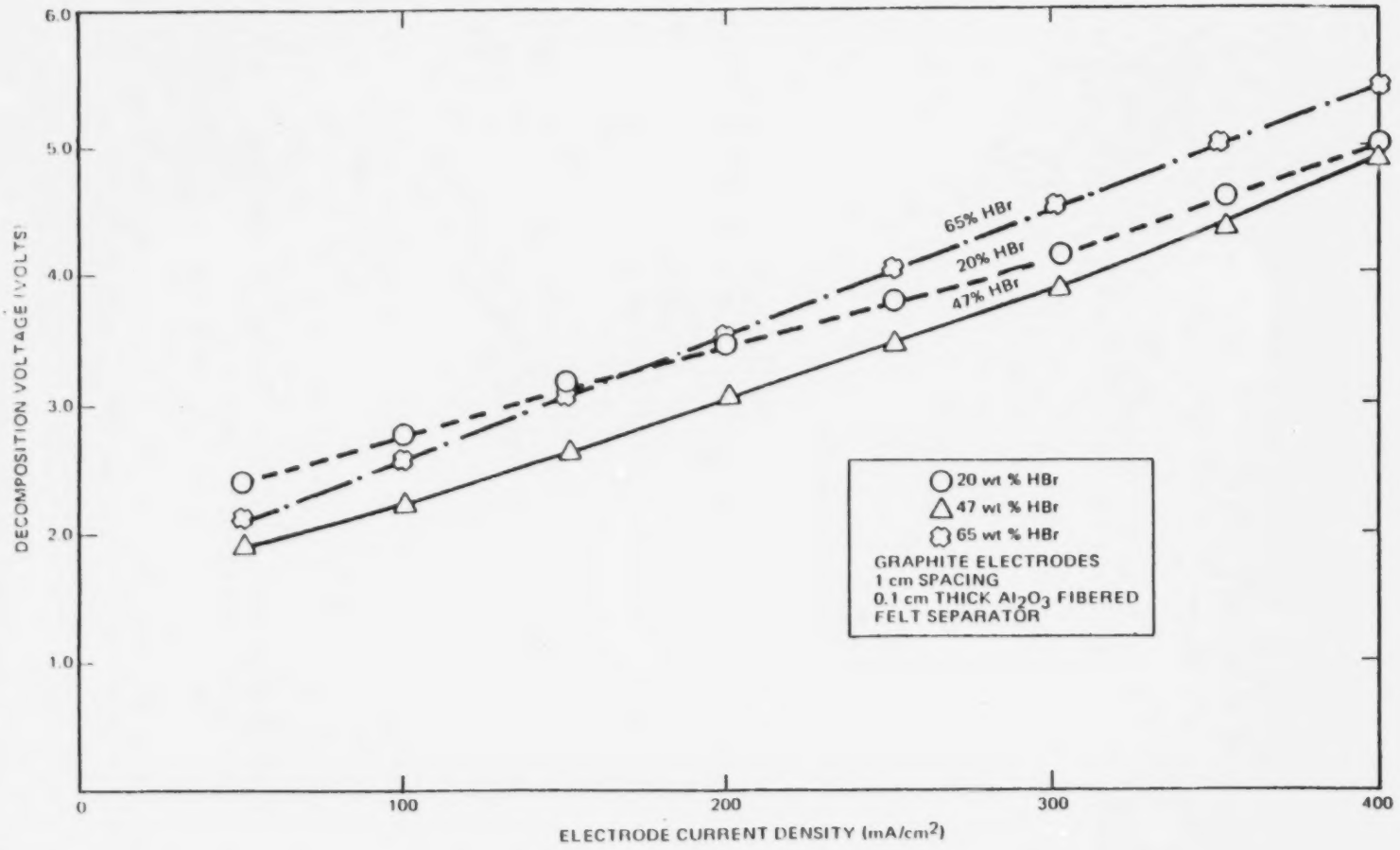


Figure 3. Decomposition Voltage of a 20, 47, and 65 wt % Aqueous HBr Solution at 25°C vs Electrode Current Density

SECTION 6

TASK II RESULTS

OBJECTIVES

Bromination

The primary objective of the bromination studies was to scale up the bromination reaction to a pilot-scale operation, in order to determine the effectiveness of the bromination reaction for the destruction of the hazardous chemical, when mixed with debris such as sand, soil, humus, and moisture.

Additional objectives were to investigate, on a laboratory scale, parameters affecting the degradation of the hazardous chemical such as mixing or stirring, reaction of the hazardous chemical with bromine dissolved in dilute HBr (in contrast to the laboratory studies carried out in Task I in which the initial reactants were water and bromine), analysis of the reaction residues to determine the extent of the reaction of Br_2 and/or HBr with the debris components, and methods for the recovery of this bromine.

Electrolysis

The primary objective of the bromine regeneration portion of Task II was to scale up the HBr electrolysis apparatus to a pilot-scale unit for regeneration of bromine from aqueous HBr. Studies were to be conducted with aqueous HBr solutions made from the bromination of hazardous chemicals. The electrolysis studies performed in Task I were conducted with synthetic HBr-H_2O solutions. Therefore, the objective of Task II was to conduct studies to determine the effect of other ions, e.g., chloride, sulfate, and phosphate (present in the HBr solutions prepared from the bromination of hazardous chemicals) on the electrolysis of HBr.

Engineering

The objective of the engineering studies was to take the data generated in Tasks I and II of this program and pertinent data available from the literature, and prepare a conceptual design of a system for disposal of spilled hazardous carbonaceous chemicals by the Rockwell bromination process. Another objective was to make an estimate of the capital cost of this system.

RESULTS

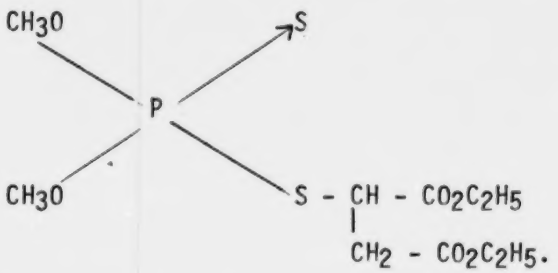
Laboratory Bromination Tests

The laboratory bromination studies carried out in Task I were scaled up approximately tenfold in size, as an intermediate step. This approach allowed testing to be carried out on an expanded scale by modification of the existing laboratory apparatus used in Task I, while the pilot-unit bromination apparatus was being constructed. These intermediate-size bromination reaction tests were performed to study (1) effects of experimental changes, such as mixing or stirring, on the bromination reaction rate, (2) the effect of debris on the reaction of the spilled hazardous chemical, and (3) the extent of the reaction of bromine and/or hydrobromic acid with debris components, which might be present with the hazardous spilled chemical.

Test Materials

Malathion ($C_{10}H_{19}O_6PS_2$) was selected in conference with the EPA Project Officer as a typical hazardous chemical for the Task II studies.

Malathion's [S-(1,2-dicarbethoxyethyl) O,O-dimethyl phosphorodithioate] structural formula is:



Malathion is a contact insecticide used to kill a variety of insects. It has a melting point of 3.7°C and a boiling range of 156° to 175°C (at 0.7 atm). It has only limited solubility in water (145 ppm at 25°C) and is completely soluble in most organic solvents. It has a specific gravity of 1.24 at 25°C and a viscosity of 36.8 cp at 25°C.(3)

Analytical reagent grade (98% pure) Malathion was obtained from the American Cyanamid Company for these tests. Simulated spill mixtures were made up of 70 wt % Malathion mixed with 30 wt % debris, consisting 10 wt % sand, 10 wt % soil, 5 wt % humus, and 5 wt % moisture.

Experimental

The tests were performed in 600-cc sealed glass ampules, which in turn were contained within a 2000-cc steel autoclave. A small amount of water

was placed in the steel autoclave to partially balance the vapor pressure of the H_2O-Br_2-HBr components within the glass ampule. The apparatus is shown in Figure 4. In Task I tests, the quantity of hazardous chemical used yielded about 1 atm of CO_2 upon complete reaction. Scale up in the same apparatus was accomplished by increasing the amounts of reactants by about tenfold and permitting the CO_2 pressure to increase to about 10 atm. After the reaction was completed, the steel autoclave was chilled in liquid nitrogen to condense the CO_2. The autoclave was opened, and the tip of the glass ampule was opened.

Analyses for Malathion residues were performed on the gas phase from the reaction. A gas chromatograph was used with a flame photometric analyzer, which contained a filter and photomultiplier detector sensitive to phosphorus emission. Thus, the test was specific for phosphorus-containing residuals. Following this, an electron capture detector was used in conjunction with the gas chromatograph to increase the sensitivity of the analytical method. Analyses of the liquid phase for Malathion residuals were also performed by a gas chromatographic technique, after an extraction from the liquid phase with petroleum ether. Blank tests were run to show that the method was effective in extracting the Malathion from an aqueous HBr solution. The solid residue from the bromination reaction of Malathion mixed with debris (the only test yielding a solid residue) was also analyzed for Malathion. This analysis was carried out by first filtering the solid residue from the solution and rinsing it with hydrobromic acid. Hydrobromic acid (47 wt % HBr) was then added to the residue, and the mixture was refluxed at 127°C for 30 min. The HBr extract was cooled and then extracted with petroleum ether. The petroleum ether extract was analyzed for Malathion by gas chromatography in the same manner as described above.

Effect of Dissolved Br_2 and Debris

Scaled-up bromination tests were performed with Malathion in the apparatus shown in Figure 4, at a temperature of 300°C for 5 hr, using 5 wt % excess bromine, under three different conditions: (1) control tests in which the amounts of reactants were increased about tenfold but with conditions (temperature, stoichiometry) identical to those used in the Task I studies (this was done to determine the effect of a tenfold scale-up on the effectiveness of destruction of Malathion); (2) tests in which the initial reactant was bromine dissolved in 22 wt % aqueous HBr* (this condition approximates the initial concentrations of the reactants in the pilot-scale tests to follow); and (3) tests with the bromine dissolved in 22 wt % HBr (as in 2) but in which the Malathion (70 wt %) was mixed with debris composed of 10 wt % sand, 10 wt % soil, 5 wt % humus, and 5 wt % moisture to more closely approximate the conditions which might occur in the disposal of a spilled hazardous chemical.

*The water for the reaction in this case was provided by the 22 wt % HBr aqueous solution. The acid concentration upon completion of the reaction was 38 wt % HBr.

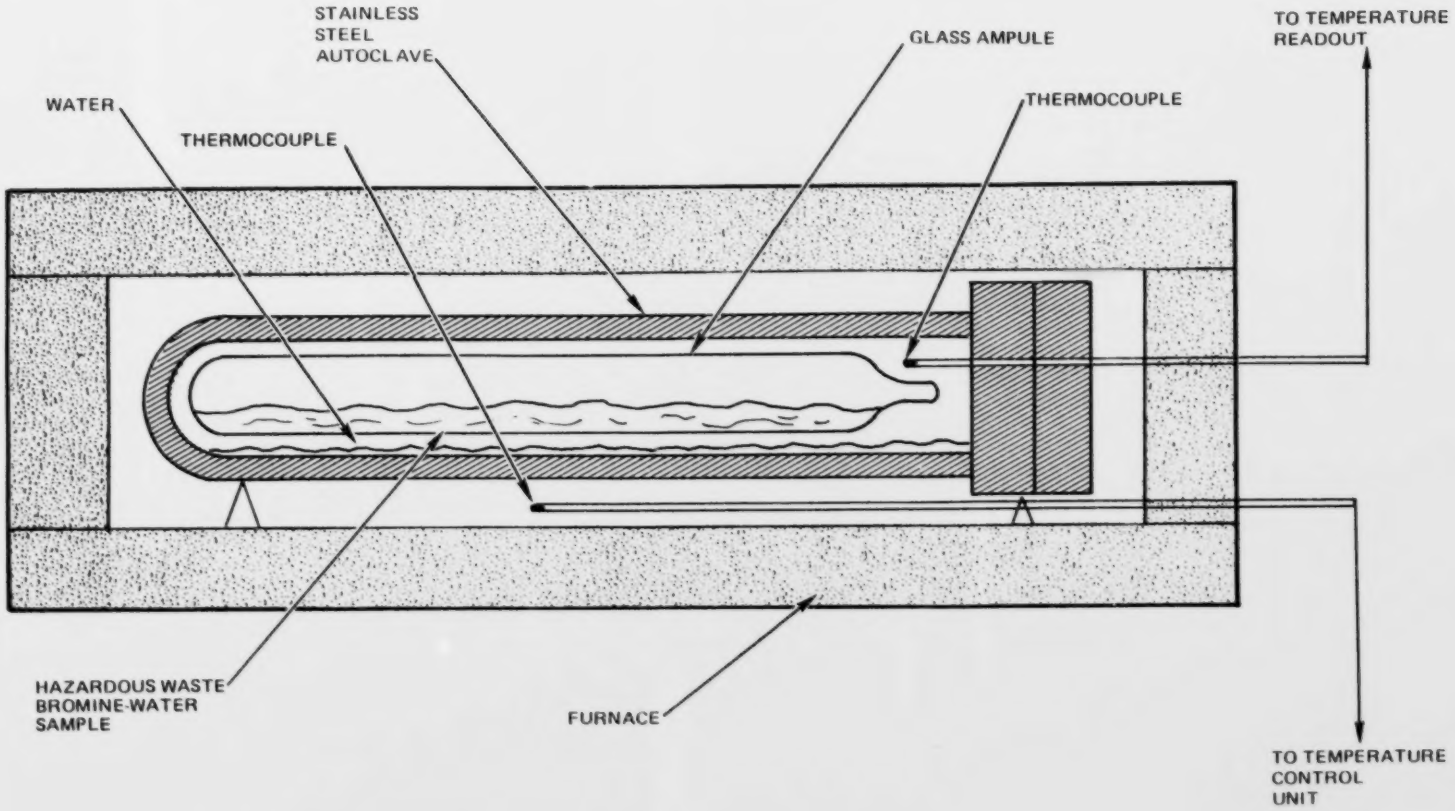


Figure 4. Laboratory Bromination Vessel

The gaseous, liquid, and solid (solid residues were observed only when samples of malathion mixed with solid debris were tested) products were analyzed by the gas chromatographic techniques described above. No phosphorus-containing organic residuals were detected in the gaseous, liquid, or solid products from the above three tests. Tests with known standards showed that the concentration of malathion or other phosphorus-containing organic products in the gas phase was < 0.3 mg/l, < 0.0007 microgram (ug)/l for the liquid phase, and < 2 microgram (μg)/g for the solid residue.

The results from the malathion residual analyses of the gaseous, liquid, and solid phases from the bromination tests with malathion are given in Table 1. In each case, the bromination reaction was effective in destruction of malathion to the extent of $\geq 99.9998\%$.

TABLE 1. MALATHION RESIDUALS FROM BROMINATION REACTION

	Concentration of Residual Malathion			
	Gas Phase (mg/l)	Liquid Phase (ug/l)	Solid Phase (ug/g)	Malathion Destruction (%)
Malathion reacted with bromine and water	ND+, <0.3	ND, <0.0007	*	>99.9999
Malathion reacted with bromine dissolved in 22 wt % HBr	ND, <0.3	ND, <0.0007	*	>99.9999
Malathion mixed with 30% debris, then reacted with bromine dissolved in 22 wt % HBr	ND, <0.3	ND, <0.0007	2	>99.9998

* No solid phase was observed
\+ ND - Not detected

Effect of Agitation

Tests were performed to determine the effect of agitation of the reactants on the reaction rate of malathion with bromine and water. These tests were performed in the apparatus shown in Figure 4. Control tests were carried out with the apparatus maintained in a horizontal, static position. Similar tests were then performed in which agitation was accomplished by rotating the autoclave (containing the malathion sample) and furnace assembly, in an oscillatory motion 30^{o} above and below horizontal, at three cycles per minute. This caused the reactants to run or flow from end to end of the glass ampule. The extent of reaction of malathion with agitation is compared with data without agitation in Table 2.

TABLE 2. EFFECT OF AGITATION ON REACTION OF MALATHION WITH BROMINE AND WATER(a)

Reaction Time (hr)	Amount of Malathion Reacted: Without Agitation (%)	Amount of Malathion Reacted: With Agitation (%)
1	85(b)	98.3 +0.3(b)
2	89(b)	>99.9999(c)
2	89(b)	>99.9999(c)
5	>99.999(c)	

a Reaction with an initial Br_2/H_2O/malathion mole ratio of 40/600/1.

b From analyses of HBr, H_2SO_4, and H_3PO_4 formed.

c From analysis of malathion residuals by gas chromatography.

Residues were visible in the tests carried out for 1 and 2 hr without agitation. A small amount of solid residue was visible in the test conducted for 1 hr with agitation. No residue was visible in the 2-hr tests with agitation or the 5-hr test without agitation. The two solutions from the tests carried out for 2 hr with agitation and for 5 hr without agitation were analyzed by gas chromatography. These analytical results showed agitation reduced the time required for destruction of the malathion from 5 hr to about 2 hr.

Reaction of Bromine with Debris

It is likely that a spilled hazardous chemical will also contain debris such as sand, soil, humus, and moisture. Consideration was given to reaction of bromine with such debris components, since these reactions will probably consume bromine and may also put soluble, nonvolatile metallic bromides into the HBr electrolyte. The metallic bromides must be removed from the HBr solution and disposed of. Qualitative tests with a malathion-debris mixture showed that the HBr solution contained nonvolatile bromides. This was determined by evaporating some of the solution to dryness. In tests where debris was present, a nonvolatile residue was observed, whereas no residue was observed in tests from the reaction of malathion alone.

Bromination tests were conducted with sand, soil, and humus for 5 hr at 300°C to determine the extent of reaction with bromine. The amounts of bromine reacted with the debris components are shown in Table 3.

TABLE 3. AMOUNT OF BROMINE REACTED WITH DEBRIS IN 5 HR AT 300°C

Component	Bromine Reacted * (g Bromine/g of Debris Component)
Sand	0.04
Soil	0.11
Humus	4.74

* For comparison, 15.5 g of bromine reacted for each gram of Malathion consumed

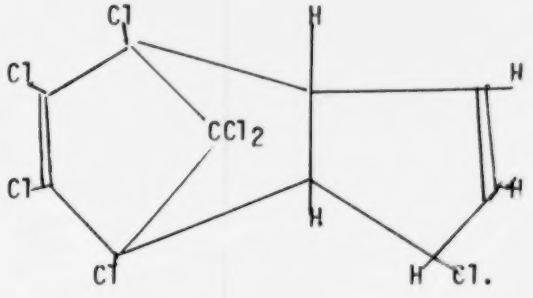
Approximately 90% of the bromine which reacted with humus formed HBr, which can subsequently be regenerated by electrolysis. The inorganic components of the debris also reacted with bromine to form metal bromides. These bromides, unlike HBr, are not regenerated in the electrolysis step. However, it was demonstrated in laboratory tests in Task I[1], that the bromine from these bromides can be recovered by treatment of the residue with sulfuric acid at 110°C. This converts the metal bromides (MBr)* to hydrogen bromide and metal sulfates:

$$2MBr + H_2SO_4 \longrightarrow 2HBr + M_2SO_4.$$

The resulting hydrogen bromide can be electrolyzed to recover the bromine. The bromine recovery tests indicated that treatment of the inorganic bromides with sulfuric acid would reduce the bromine loss to about 0.1 kg/metric ton of spill mixture treated.

Chlorinated Hydrocarbons

At the suggestion of the EPA Project Officer, bromination tests were carried out with two chlorinated hydrocarbons, Lindane and Heptachlor, to determine the extent of degradation by bromine and water. Lindane is the gamma or "chair" structural isomer of hexachlorocyclohexane ($C_6Cl_6H_6$). Heptachlor ($C_{10}H_5Cl_7$) has the following structural formula:



* A monovalent metal is used for purposes of this illustration.

Laboratory-scale bromination tests were performed with Lindane and Heptachlor in the apparatus described in the section on Task II results. Reaction for 1 hr at 280°C yielded 46% and 56% of the amount of HBr expected from complete degradation of the carbon and hydrogen in the respective compounds. The HBr yields from these tests were less than the HBr yields from the tests carried out in Task I with trichloroethane under similar experimental conditions.[1] Bromination tests for 1 hr at 300°C resulted in HBr yields of 56% and 71% for Lindane and Heptachlor, respectively. These cyclic chlorinated compounds are, thus, more resistant to the degradation/oxidation by bromine than the aliphatic chlorinated compound trichloroethane.

Pilot-Scale Bromination Tests

Procurement and Testing of Reaction Vessel

One of the goals of Task II was to scale up the laboratory bromination reaction studies carried out in Task I by about a hundredfold with a simulated spill mixture in order to determine the effectiveness of destruction of the hazardous chemical.

These tests were originally scheduled to be performed in a procured 8-liter (2-gal) tantalum-plated autoclave. However, corrosion tests conducted at the beginning of Task II showed that HBr and/or Br_2 penetrated the tantalum plating and attacked the underlying stainless steel vessel walls. Control tests performed with 0.13-cm-thick tantalum sheet stock with HBr and Br_2 under identical conditions of concentration and temperature indicated that the corrosion rate of the tantalum sheet was of the order of only about 0.013 cm/yr. This indicated the tantalum plating was defective and was not protecting the underlying stainless steel vessel. This was probably due to the dendritic crystal structure of the plated tantalum which tends to be mechanically unstable. Temperature cycling tends to break off dendrites from the tantalum plating due to the differential coefficient of expansion between the tantalum and the underlying stainless steel. The numerous pits or "pockmarks" observed on the surface of the tantalum-plated vessel after exposure to hydrobromic acid tend to support this view.

On the other hand, the corrosion tests with the tantalum sheet were encouraging since the corrosion rate with HBr/Br_2, even at 300°C, was acceptable from an engineering standpoint. A new 8-liter autoclave replacement vessel, with a 0.13-cm-thick tantalum lining, was procured from a different vendor to carry out the pilot-scale bromination reaction tests. Upon receipt of this new vessel, corrosion tests were performed with a HBr/Br_2 aqueous solution at 300°C. Chemical analyses and visual inspection of the autoclave indicated no detectable corrosion of the underlying steel vessel and that the corrosion rate of the tantalum lining, on the average, was less than 0.008 cm/yr. Thus, these corrosion tests, under simulated operating conditions, indicated the tantalum-lined vessel was satisfactory for carrying out the pilot-scale bromination tests.

Description of Pilot-Scale Bromination System

A pilot-scale bromination system was constructed using the 8-liter tantalum-lined autoclave, a steam generator for injection stirring, valves, temperature controls, and a pressure gauge. The autoclave had an internal diameter of about 15 cm with a depth or length of about 45 cm. The autoclave was designed for operation at 17,000 kPa pressure at a temperature of 300°C. The autoclave walls were made of approximately 2.54-cm-thick carbon steel. The autoclave was totally lined with 0.13-cm-thick tantalum sheet. The lid or cover was also tantalum lined with tantalum-lined parts for connection of the autoclave to the other parts of the system. A schematic diagram of the apparatus is shown in Figure 5. A Bourdon gauge was attached to the autoclave (isolated from the HBr/Br_2 vapors by means of a tantalum diaphragm) for monitoring the CO_2 pressure within the system. The autoclave was equipped with a pressure relief valve and a remote-controlled vent valve. Stirring of the reactants was accomplished by means of a tantalum sparge tube connected to a steam generator through a check valve and a remote-controlled steam injection valve. The steam generator was also equipped with a Bourdon gauge, pressure relief, and remote-controlled vent valves. The autoclave was heated by a five-zone band heater assembly, each separately monitored by a thermocouple sensor. The power to each heater was controlled by a solid-state controller. The steam generator was also equipped with similar temperature monitoring/control units. A schematic drawing of the pilot-scale bromination reaction test installation is shown in Figure 6. A photograph of the autoclave assembly is shown in Figure 7. The temperature control unit is shown in Figure 8.

Test Results

Following solution of some corrosion problems encountered in a preliminary test, a successful bromination test was conducted using a simulated hazardous chemical spill mixture consisting of 35 g of Malathion mixed with 15 g debris, which consisted of 5 g of soil, 5 g of sand, 2.5 g of humus, and 2.5 g of moisture. Bromine was used in 5% excess of the amount for complete reaction of the Malathion-debris mixture.* The reaction was carried out for 2 hr at 300°C. During the first hour at this temperature, the pressure in the autoclave increased. This pressure increase was attributed to the generation of CO_2. After approximately 1 hr at 300°C, the pressure in the system remained constant at 7521 kPa. The system was held at this constant temperature and pressure for 1 hr to give the Malathion the opportunity to react completely. The autoclave was then cooled to ambient temperature. The pressure in the autoclave at ambient temperature was 1208 ±34 kPa. The pressure of CO_2 expected from complete reaction of the Malathion-debris mixture used in this test was calculated to be 1159 kPa, thus indicating essentially 100% reaction of the Malathion-debris mixture. Samples were taken of the gaseous CO_2

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*15.5 g of Br_2 are required for reaction of each gram of Malathion; 4.9 g of Br_2 for each gram of debris.

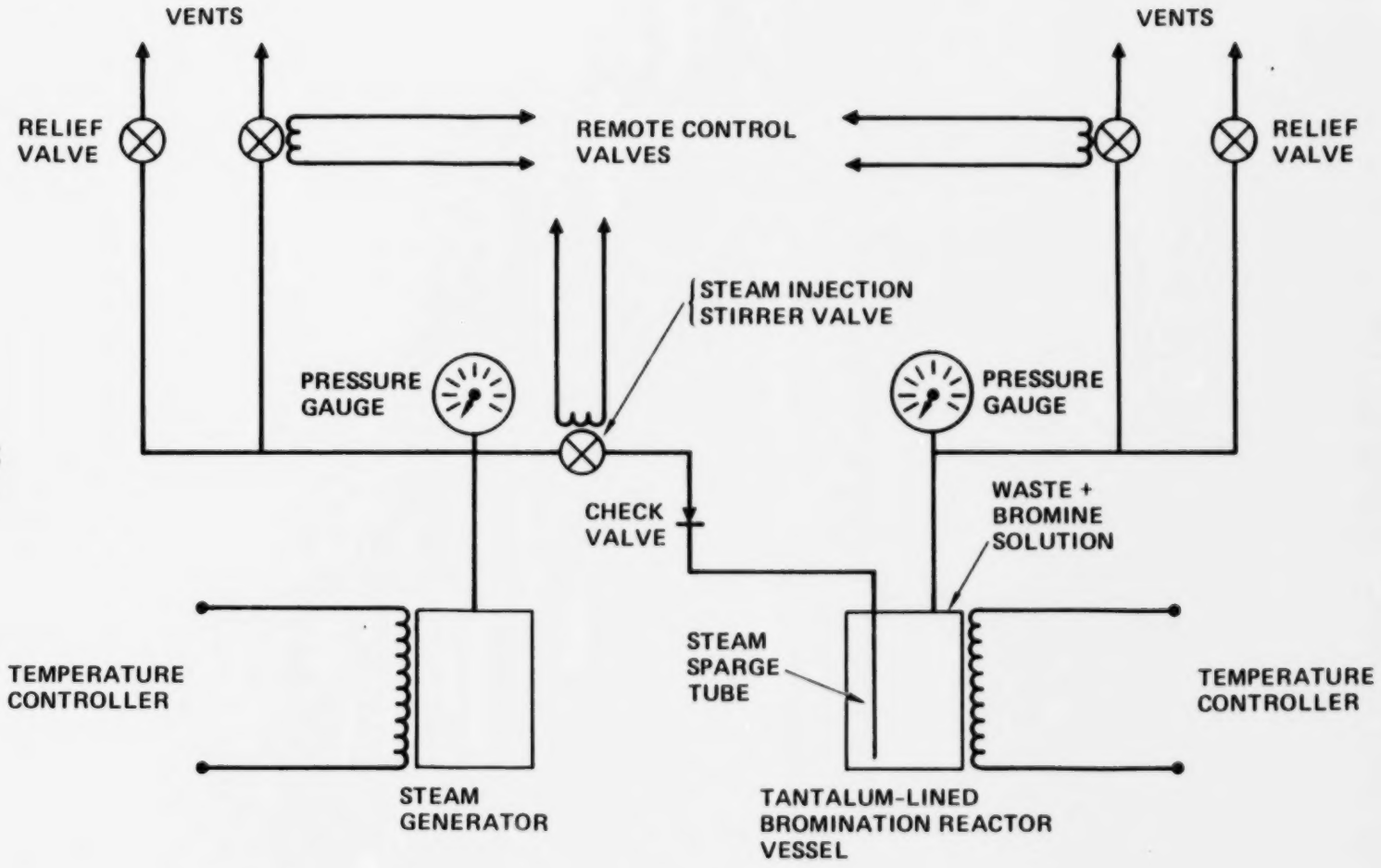

Figure 5. Schematic Diagram of Pilot-Scale Bromination System

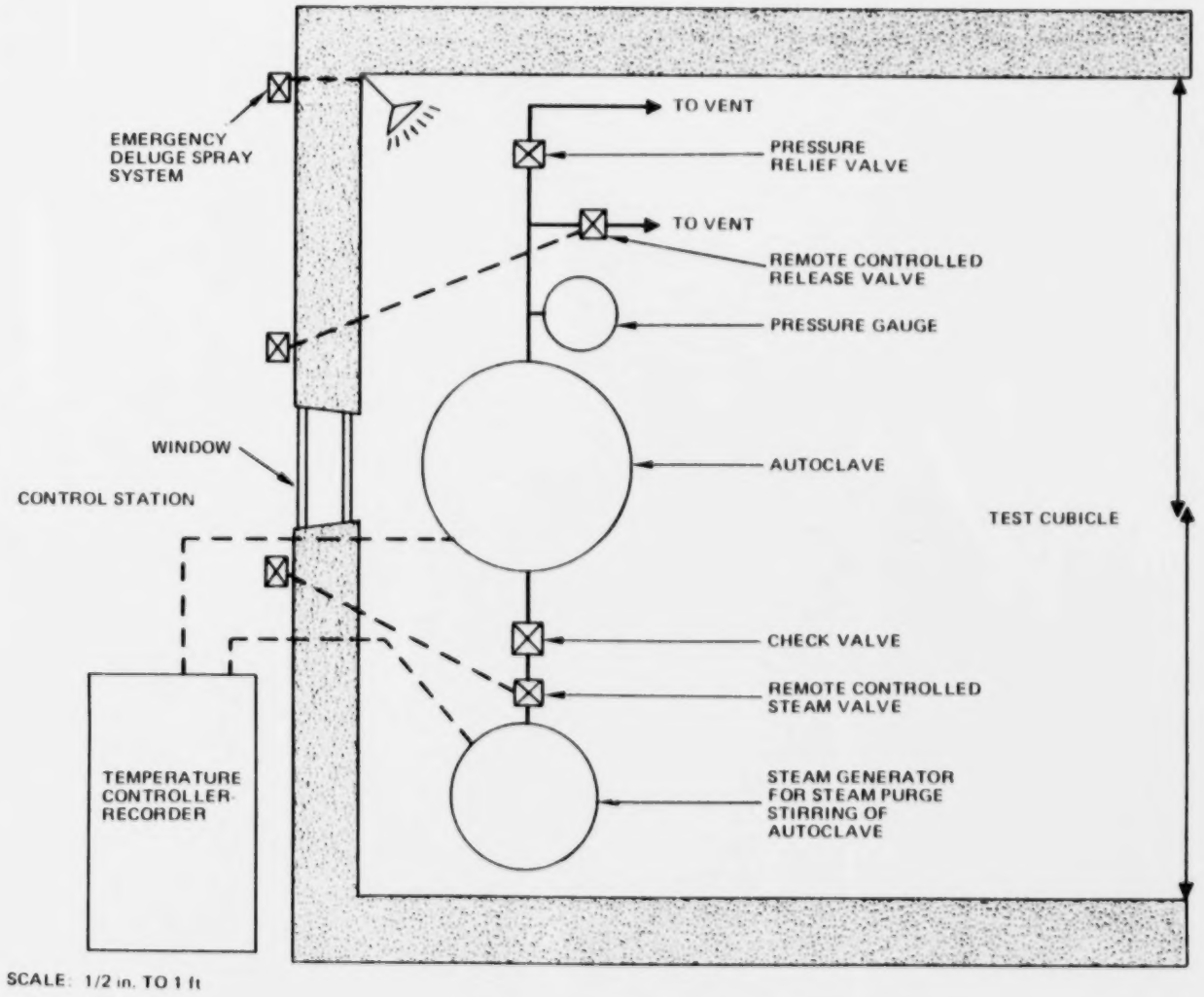

Figure 6. Schematic Drawing of the Pilot-Scale Bromination Reaction Test Installation

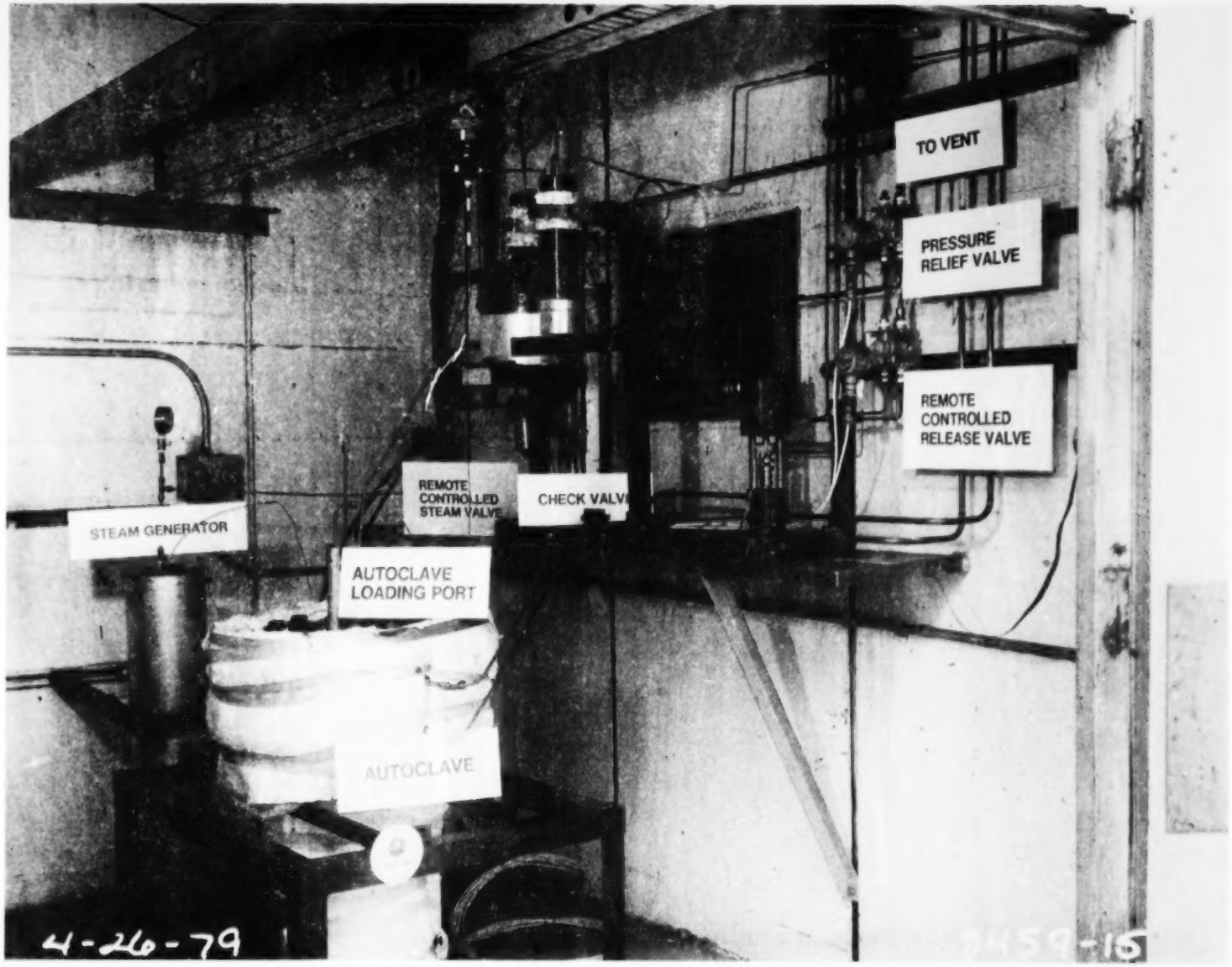

Figure 7. Autoclave Assembly, Pilot-Scale Bromination Reactor

Figure 8. Temperature Control Unit, Pilot-Scale Bromination Reactor

and of the HBr solution. The gaseous CO_2 was then scrubbed (by passing it through a caustic solution) and released to the atmosphere. The solid residue or unreacted debris was rinsed with caustic solution and discarded. The concentrated HBr aqueous solution (38 wt % HBr) was stored for use in the pilot-scale electrolysis tests. Analyses for Malathion residuals were performed on the gaseous and liquid products to determine the effectiveness of the scaled-up bromination reaction for destruction of Malathion. The analyses of the products were carried out using the gas chromatographic analysis technique described earlier.

The results from this test are summarized in Table 4. They show that the destruction of Malathion was $\geq$99.9999% complete. No Malathion residuals were detected in the gaseous, liquid, or solid products from this test. The limit of detection of Malathion in the gaseous sample was 0.5 ppm; the limit of detection of Malathion in the liquid sample was 0.5 ppb.

In summary, the 8-liter pilot-scale bromination reactor apparatus gave greater than 99.9999% destruction of the Malathion in hundredfold scale-up in size from the laboratory tests under similar conditions of time (2 hr) and temperature (300°C). Furthermore, the pressure of the gaseous CO_2 product generated in situ by the reaction gave an indication of the progress or extent of the reaction during the test.

Laboratory Electrolysis Tests

Test Materials

Laboratory-scale tests were continued in the Task II studies to determine the effect of other ions such as cupric (Cu^{++}), chloride (Cl^-), sulfate ($SO_4^=$), and phosphate ($PO_4^{\equiv}$), on the electrolysis of HBr solutions. The electrolytes for these tests were obtained by reacting bromine and water with: (1) copper acetate (for Cu^{++}-containing HBr solution), (2) trichloroethane (for Cl^--containing HBr solution), and (3) Malathion (for $SO_4^=$- and $PO_4^{\equiv}$-containing HBr solution).

Apparatus

These tests were conducted using an electrolysis cell with graphite electrodes having a surface area (planar) of 14 cm^2, spaced 1.0 cm apart, and employing an Al_2O_3 fibered-felt membrane separator. The tests were conducted as a function of electrode current density at 25°C.

Test Results

The results of the electrolysis test with the solution from the copper acetate-bromine reaction are shown in Figure 9. The decomposition voltage of the 47 wt % HBr aqueous solution, containing about 1 mole of copper for each mole of HBr, was measured as a function of electrode current density and is somewhat lower than that of the reference 47 wt % HBr solution. This may be due to the higher concentration of ions in the copper-containing

TABLE 4. RESULTS OF PILOT-SCALE BROMINATION TEST

Feedstock	35 g, Consisting of: Malathion: 70 wt % Sand 10 wt % Soil 10 wt % Humus 5 wt % Moisture 5 wt %
Temperature	296°C
Duration	2 hr
CO_2 Product	Expected: 1.52 g-mol Found: 1.53 ±0.01 g-mol
HBr Product	38 wt % aqueous HBr Expected: 1.94 g-mol Found: 1.96 ±0.01 g-mol
Malathion Residuals	Gas Phase: Not detected, ≤0.5 ppm Liquid Phase: * Not detected, < 0.5 ppb
Malathion Destruction	≥99.9999%

* The solid residue was rinsed with a concentrated aqueous HBr solution. This rinse solution was then added to the liquid phase product.

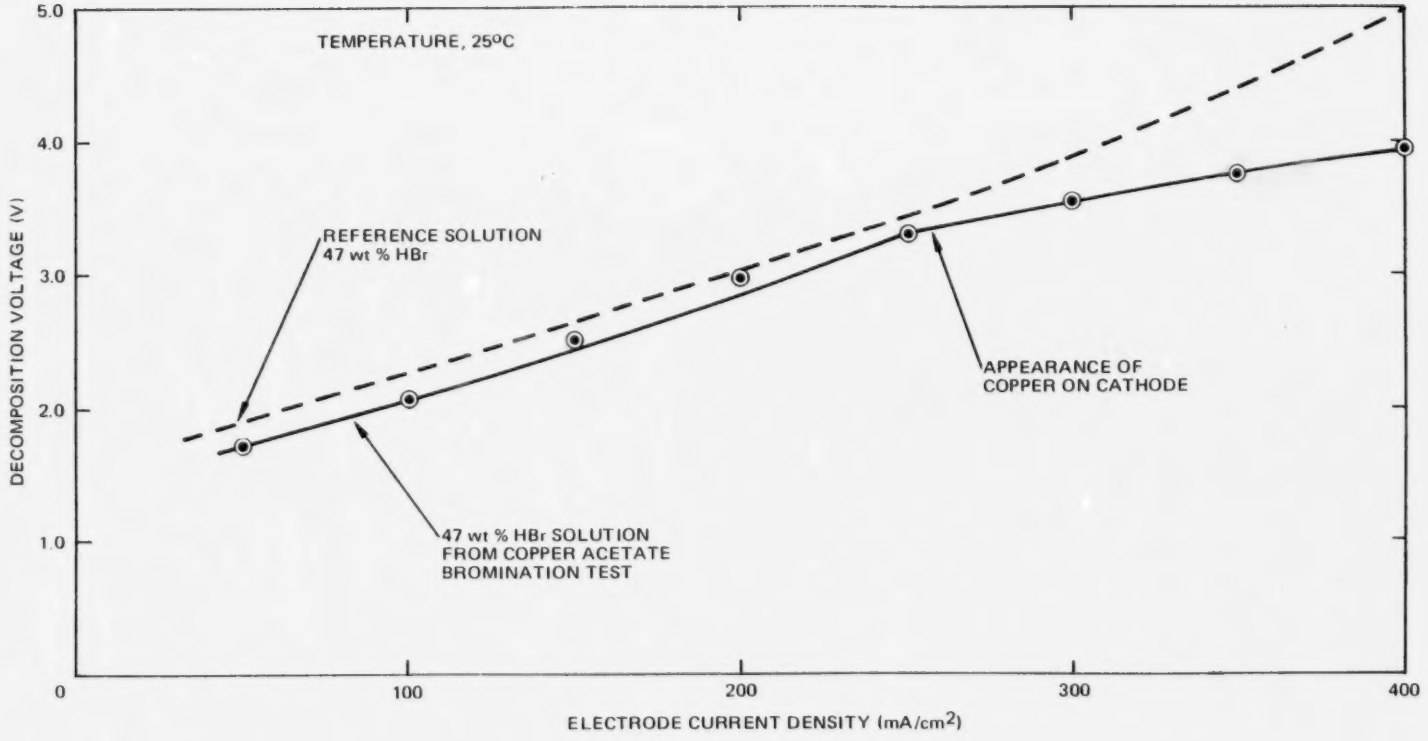

Figure 9. Decomposition Voltage vs Current Density of an HBr Solution Prepared from Reaction of Copper Acetate with Bromine and Water

solution. The observed effect could also be due to a lower electrode overpotential of hydrogen in the presence of copper ions. At a voltage of about 3.2 V, copper was visually observed to plate out on the graphite cathode. This deposition was also indicated by the change in slope of the decomposition voltage vs electrode current density curve. This, at electrode current densities below about 250 mA/cm^2, the presence of copper ions has only a small effect on the electrolysis of this 47 wt% HBr solution. Final removal of the copper would be brought about by electrolyzing the copper from the solution, then discarding the copper metal.

Similar studies were conducted with the HBr solutions from the reaction of trichloroethane with bromine and water. In this case, 3 moles of HCl were formed per 8 moles of HBr. The decomposition voltage of the resulting HBr/HCl solution was measured as a function of electrode current densities from 50 to 400 mA/cm^2. These results are compared in Figure 10 with the decomposition voltage versus current density for a reference solution containing only HBr (at the same HBr concentration, 43 wt%).* The decomposition voltage of the HBr/HCl solution is approximately 10% lower than that of the reference 43 wt% HBr solution over the entire range of current densities studied. The lower decomposition voltage of the HBr/HCl solution under load conditions is attributed to the higher electrical conductivity of this solution as compared to the reference HBr solution, thus yielding a lower IR drop between the electrodes. No chlorine was evolved since the decomposition potential (E_o) of HCl is approximately 0.5 V higher than that of HBr. Final disposal of such HBr/HCl solutions is made after electrolysis of the HBr. This is accomplished by using gaseous chlorine to strip out any remaining bromide, i.e., $Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$, followed by neutralization of the remaining HCl with lime, then discarding the resulting $CaCl_2$ solution at a suitable site.

Similar studies were conducted with HBr solutions from the reaction of Malathion with bromine and water. In this case, 2 moles of H_2SO_4 and 1 mole of H_3PO_4 were formed for each 64 moles of HBr. The results from the electrolysis tests with this solution are shown in Figure 11. In this case, the decomposition voltage of the 47 wt% HBr aqueous solution from the bromination of Malathion is higher than that of the reference 47 wt% HBr solution. The sulfate ($SO_4^=$) and/or phosphate ($PO_4^{\equiv}$) ions would be expected to change** the transport properties of the solution. However, this would be expected to cause the two curves to diverge at higher current densities. Since the two curves are converging with increasing current density, the observed effect is probably due to a change in the electrode overpotential as a result of the presence of sulfate and/or phosphate ions.

Final disposal of the solution after recovery of bromine by electrolysis would entail removal of residual HBr by bubbling gaseous chlorine through the solution, followed by neutralization of the sulfuric and phosphoric

* The results from similar tests with a 47 wt% aqueous HBr solution are also shown for comparison.

**Sulfate and phosphate would be expected to increase the viscosity and, thus,to decrease the conductivityof the solution. This would, in turn, increase the IR drop between the electrodes.

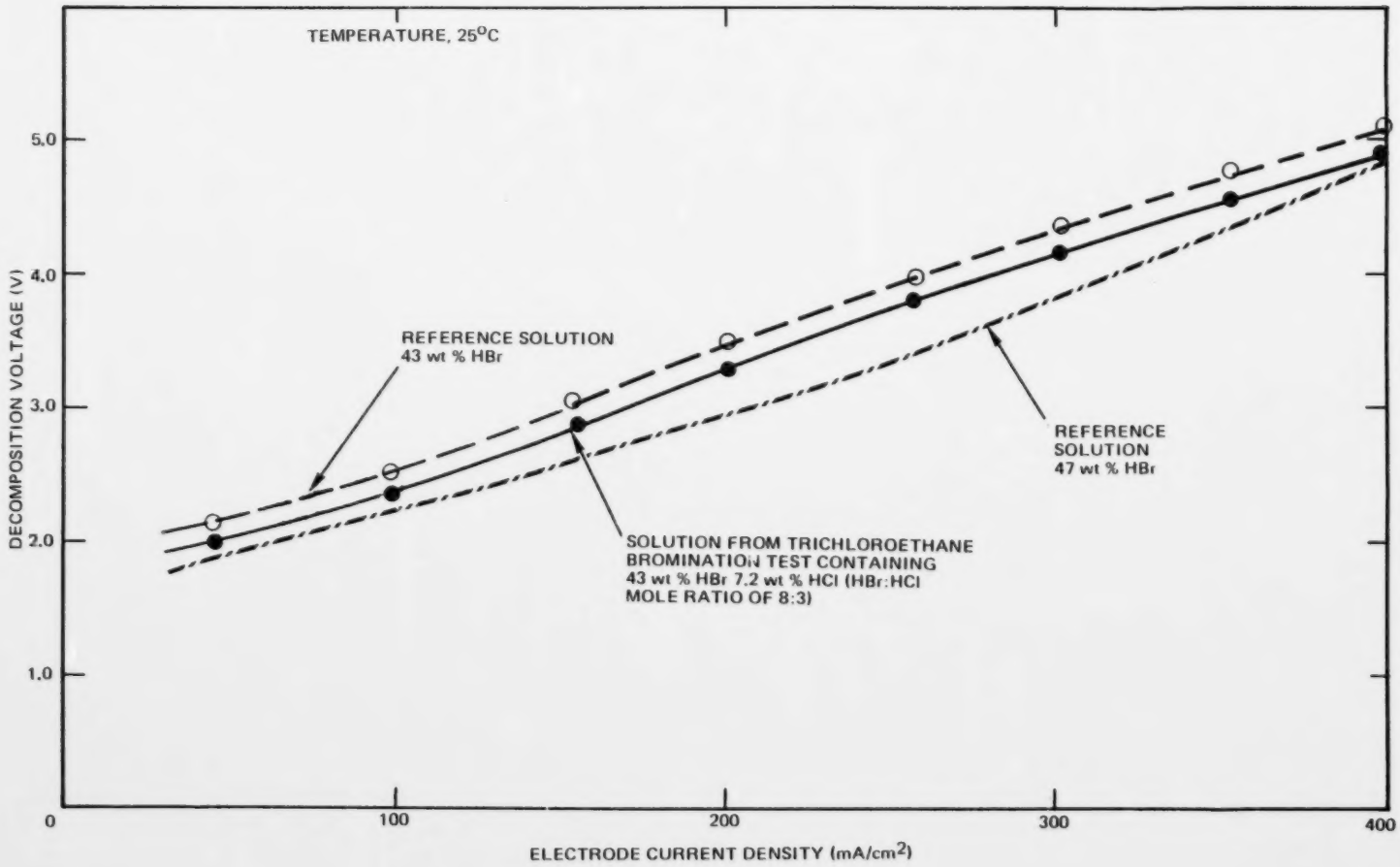

Figure 10. Decomposition Voltage vs Current Density of an HBr/HCl Solution Prepared from Reaction of Trichloroethane with Bromine and Water

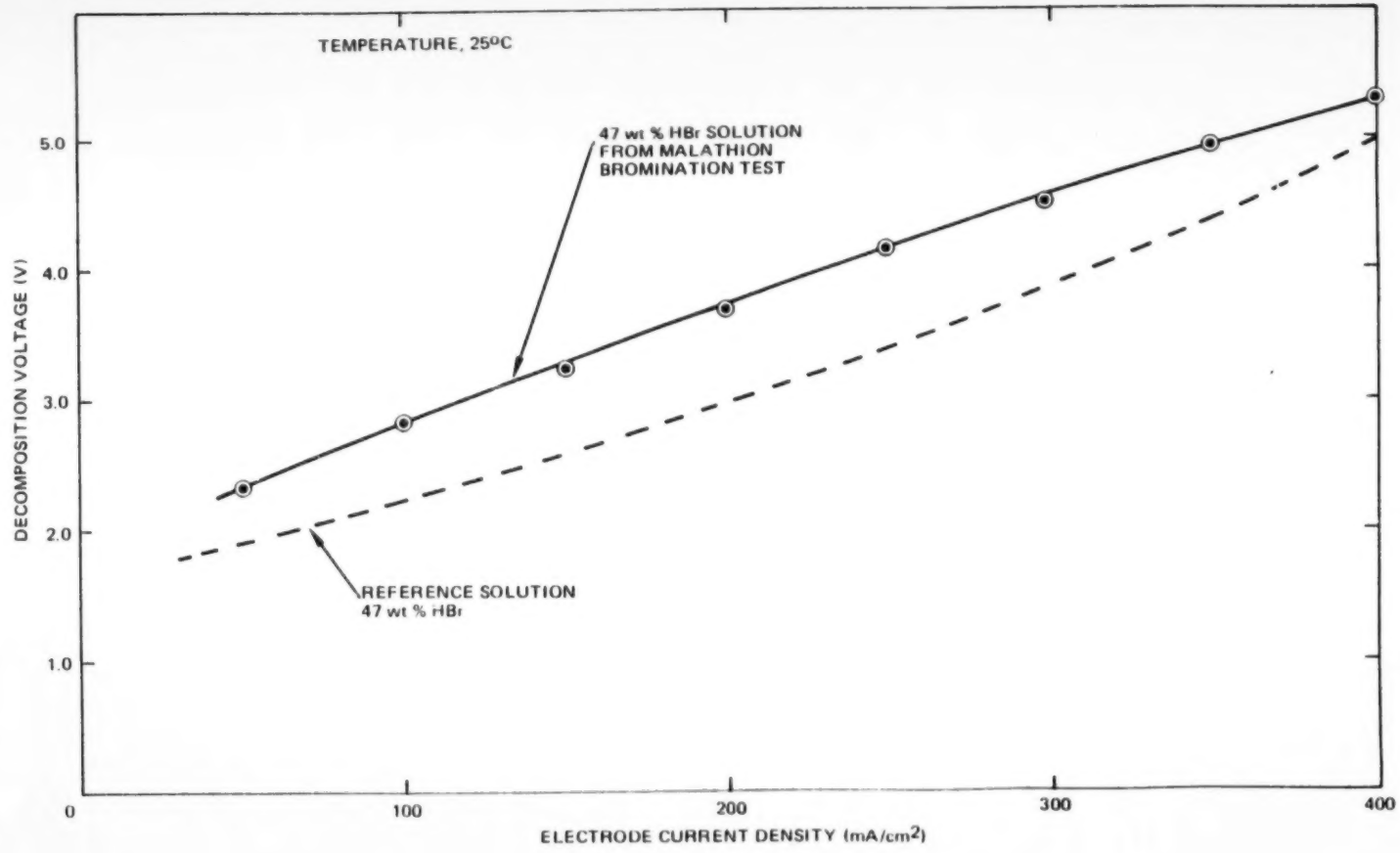

Figure 11. Decomposition Voltage Vs Current Density of an HBr Solution Prepared from Reaction of Malathion with Bromine and Water

acids with lime. The resulting calcium sulfate and phosphate are then discarded at a suitable site.

Pilot-Scale Electrolysis Tests

Four-Liter Membrane-Type Electrolysis Cell

The bromine regeneration tests described above were carried out using an electrolysis cell with an electrode surface area of about 15 cm^2. The bromine regeneration tests were then scaled up by about a tenfold factor in electrode surface area using the same basic design. The scaled-up apparatus consisted of a glass electrolysis cell approximately 15 cm (6 in.) in diameter by 30 cm (12 in.) in height (approximately 4-liter electrolyte capacity). This cell had graphite electrodes approximately 10 cm by 15 cm (150 cm^2 surface area) with an electrode spacing of 1.0 cm. The electrodes were separated by a 0.1-cm-thick Al_2O_3 fibered-felt membrane. This pilot-scale electrolysis unit is shown in Figure 12.

Bromine regeneration tests were carried out in this 4-liter electrolysis cell to determine the effect of dissolved bromine on the decomposition voltage of aqueous hydrobromic acid solutions. The tests were carried out at 25°C. The decomposition voltage was determined for (1) a 22 wt % HBr aqueous solution and (2) a 22 wt % HBr aqueous solution containing 16 wt % Br_2. The latter corresponds to the preferred composition of the effluent from the electrolysis cell in the process. The results are given in Table 5. These results are also shown in Figure 13, where the decomposition voltage is given as a function of electrode current density. It is seen that the decomposition voltage of the 22 wt % HBr solution containing 16 wt % bromine is lower than the decomposition voltage of the 22 wt % HBr solution at current densities from 50 to about 125 mA/cm^2. Similarly, Glass and Boyle, in a study of the hydrogen-bromine fuel cell system at 30°C, found that addition of bromine to a 22 wt % aqueous HBr solution lowered the no-load (i.e., current density essentially zero) decomposition potential. (2)

TABLE 5. EFFECT OF DISSOLVED BROMINE ON DECOMPOSITION VOLTAGE OF 22 Wt % HBr SOLUTION

Electrode Current Density (mA/cm^2)	Decomposition Voltage (Volts)		
	22 wt % HBr Solution	22 wt % HBr Solution Containing 16 wt % Bromine	
		Run No. 1	Run No. 2
50	2.46	2.08	2.06
100	2.77	2.63	2.59
150	3.10	3.19	3.17
200	3.42	3.82	3.74
250	3.75	4.26	4.20
300	4.16	4.62	4.61
350	4.56	5.00	5.09

*Measurements were made with solutions at 25°C using graphite electrodes spaced 1.0 cm apart and a 0.1-cm-thick Al_2O_3 fibered-felt membrane separator.

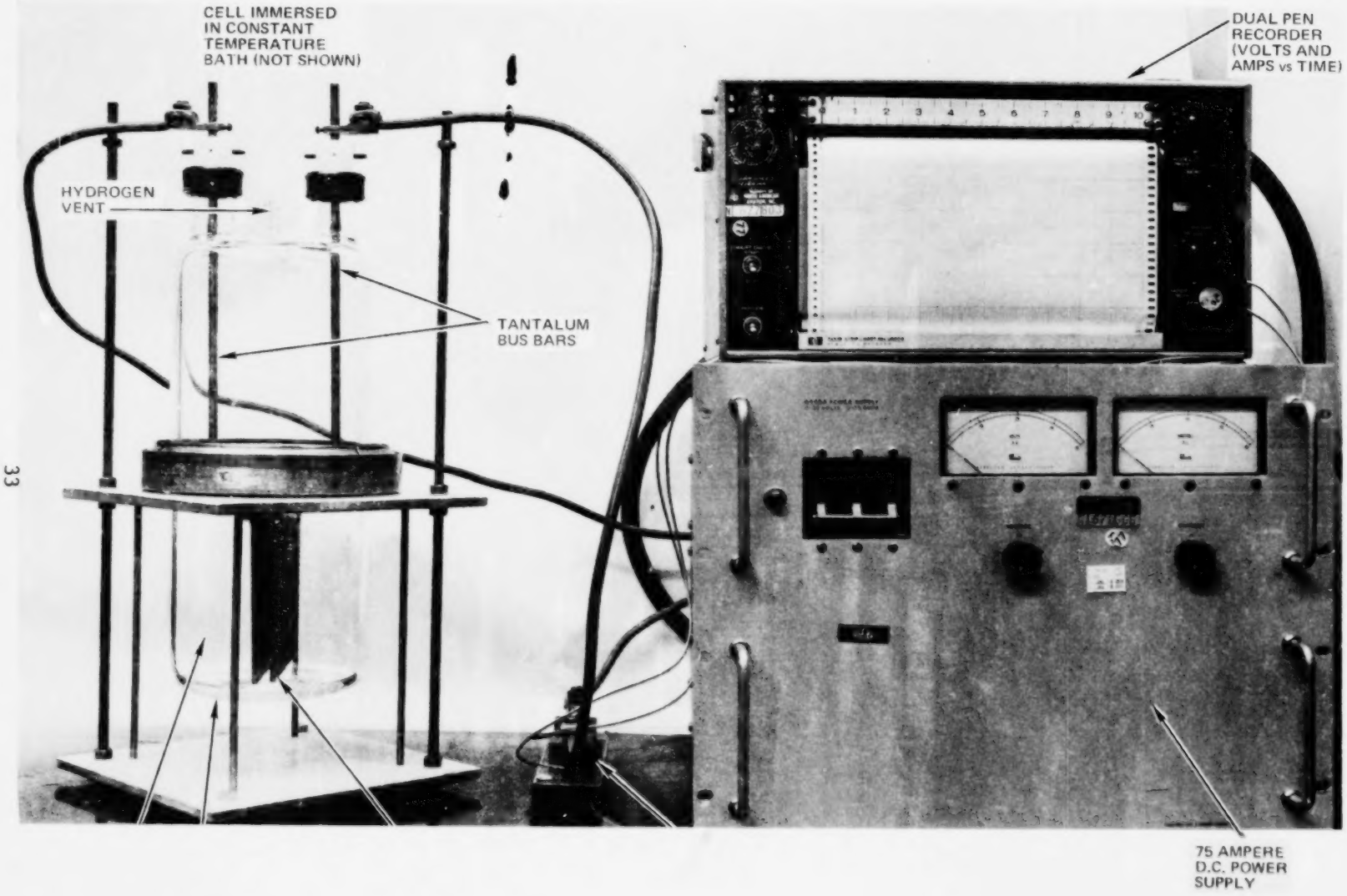

Figure 12. Four-Liter Electrolyte Capacity Electrolysis Cell

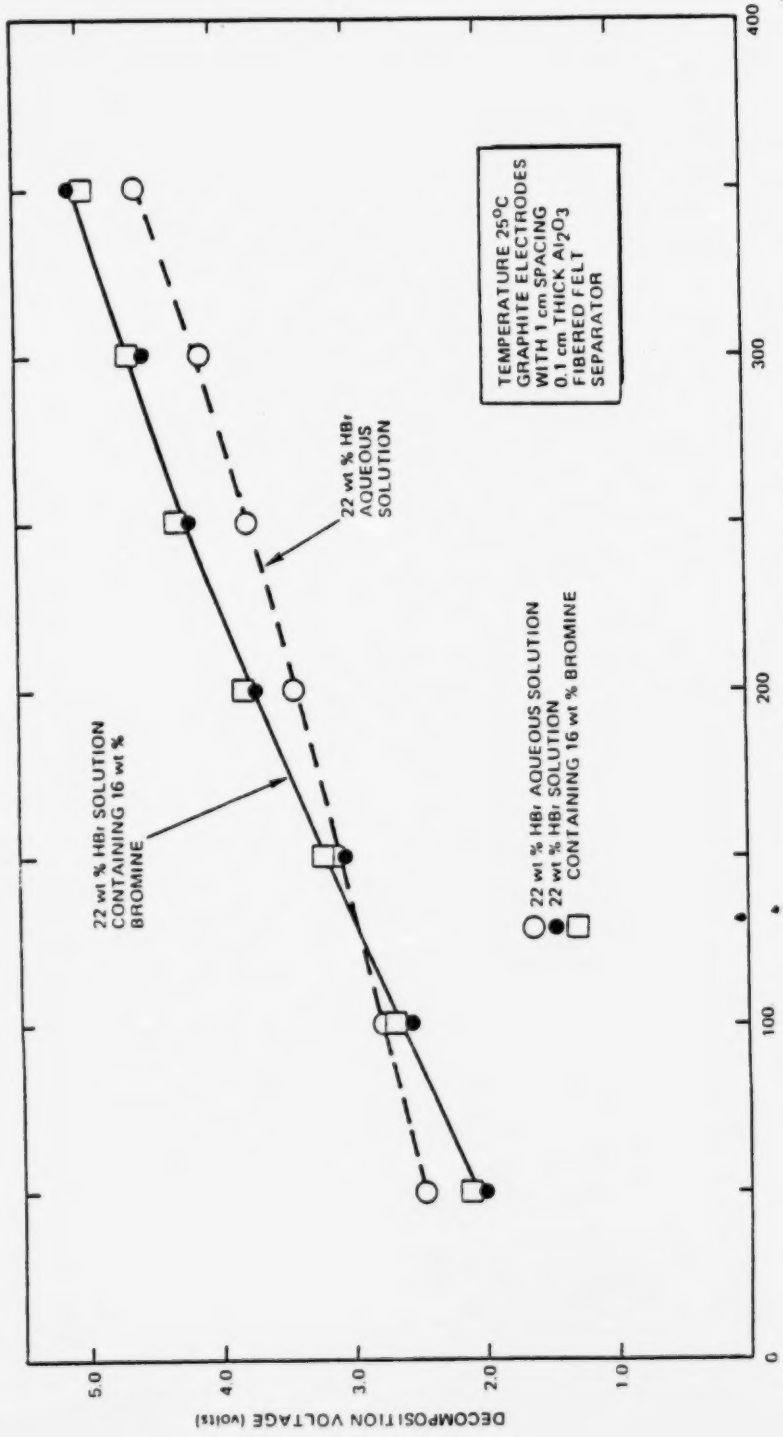

Figure 13. Effect of Dissolved Bromine on Decomposition Voltage of an HBr Solution

In these studies, the decomposition voltage of the bromine-containing HBr solution was found to increase more rapidly as a function of electrode current density than that of the HBr solution. The decomposition voltages of the two solutions are equal at a current density of 125 mA/cm^2. At higher current densities, the decomposition voltage of the bromine-containing solution is greater than that of the solution without dissolved Br_2. This can be explained in view of Glass and Boyle's work, in which it was found that dissolution of bromine in aqueous HBr solutions, decreased the electrical conductivity of these solutions.[2] This would explain the greater rate of increase in decomposition voltage of the bromine-containing solution as the electrode current density is increased.

A noticeable decrease in coulombic efficiency was observed during the electrolysis of HBr solutions containing large amounts (16 wt %) of dissolved bromine. This problem is peculiar to electrolysis of solutions, such as HBr, where one of the products (bromine) remains in solution* and diffuses through the membrane separating the anode and cathode compartments.

The Br_3^- anion sets up a competing reaction at the cathode, i.e., the reaction

$$Br_3^- + 2e^- \longrightarrow 3Br^-$$

probably occurs rather than the desired reaction,

$$H_3O^+ + e^- \longrightarrow H_2O + 1/2\ H_2.$$

The overall effect of the competing reaction is a reduction in the efficiency of the electrolysis. Diffusion of bromine through the 0.1-cm-thick Al_2O_3 fibered-felt membrane, separating the anode and cathode compartments was found to be rapid, when Br_2 concentration differences as high as 16 wt % bromine between the anode and cathode compartments were attempted. In this case, the coulombic or electrolysis efficiency approached zero. On the other hand, attempts to limit Br_2 diffusion by increasing the thickness of the separating membrane (or its density), had the undesirable effect of increasing the electrical resistance between the cathode and anode, thus increasing the electrical power loss within the cell.

Membraneless Cells

Schuetz and Lalonde have also encountered problems of diffusion of bromine through the cell membrane.[3] They suggest the use of undivided cells (i.e., cells without a membrane separator between the anode and cathode) such as have been used in industry; for example, the mercury cell for production of Cl_2 from NaCl or KCl solutions in which the alkali metal is taken up by the mercury at the bottom of the cell and the gaseous Cl_2 escapes through the anode.[4] In such a cell, the competing cathode

* In electrolysis of H_2O or HCl, for example, both products are gases and can escape from the electrolysis cell. In such cases, the membrane separating the anode and cathode compartments is effective in preventing the recombination of the two products.

reaction is minimized by controlled convective diffusion, i.e., the dissolved bromine is removed from the cell before it can diffuse to the cathode, where it undergoes electrochemical reaction. Schuetz and Lalonde found that separation of the electrodes by a few millimeters allows electrolyte residence times of several minutes, before appreciable diffusion of bromine to the cathode occurs. In studies carried out with membraneless electrolysis cells, they report electrolysis efficiencies of 95 to 100% at current densities up to 800 mA/cm^2, with bromine concentrations up to 10% at the outlet of the cell. In contrast, the coulombic efficiency of the membrane-type cell studied here was found to decrease with increasing bromine concentration of the HBr electrolyte. At 16 wt % Br_2 concentration (the concentration desired for the pilot-scale unit), the coulombic efficiency was zero, since the Al_2O_3 membrane was not effective in preventing diffusion of Br_3^- from the anode to the cathode compartments of the cell. In view of this, effort was shifted to construction of a membraneless cell using continuous flow of HBr solution through the cell. This cell is similar to the cell used in chlorine electrolysis (a well-developed technology). In addition, the capital costs of the membraneless cell is expected to be lower than those of membrane-type cells because of their simpler design.

Description of Membraneless Pilot-Scale Electrolysis Cell

In view of these considerations, a membraneless cell, which was basically similar to Schuetz and Lalonde's cell[3], was constructed; however, the electrode surface area was scaled up from 12 cm^2 used by Schuetz to 100 cm^2. Schuetz's cell was enclosed in a glass bell jar or tube, whereas our design is much simpler and more amenable to pilot-scale operation, in that it uses graphite electrodes separated by Teflon spacers. The electrodes and separators are clamped between steel plates. A schematic drawing of the cell used in this program is shown in Figure 14.

In this cell, the upper electrode serves as the cathode; the lower electrode serves as the anode. Upon passage of current through the cell, the hydrogen formed at the cathode rises along its lower surface and escapes at ports located at the upper end of the cell. Bromine formed at the anode combines with HBr to form HBr_3 (soluble in aqueous HBr), which is more dense than the HBr. This denser liquid flows through the cell along the anode surface and out of ports at the lower end of the cell. The HBr flow rate through the cell was controlled to remove HBr_3 from the cell before appreciable amounts of Br_3^- could diffuse through the electrolyte to the cathode to set up a competing electrolysis reaction.

The coulombic efficiency of this cell was measured at 25°C, with aqueous HBr flowing through the cell. The input to the cell was 38 wt % aqueous HBr. The output was HBr containing up to 10 wt % dissolved bromine (as HBr_3). The coulombic efficiency was calculated from the ratio of the amount of hydrogen electrolyzed to the amount expected based on the ampere-hours passed through the cell. The coulombic efficiency of the cell, with the electrodes inclined at an angle (a) of 16° and 3° from horizontal, and for electrode current densities of 50 and 100 mA/cm^2, is given in Table 6.

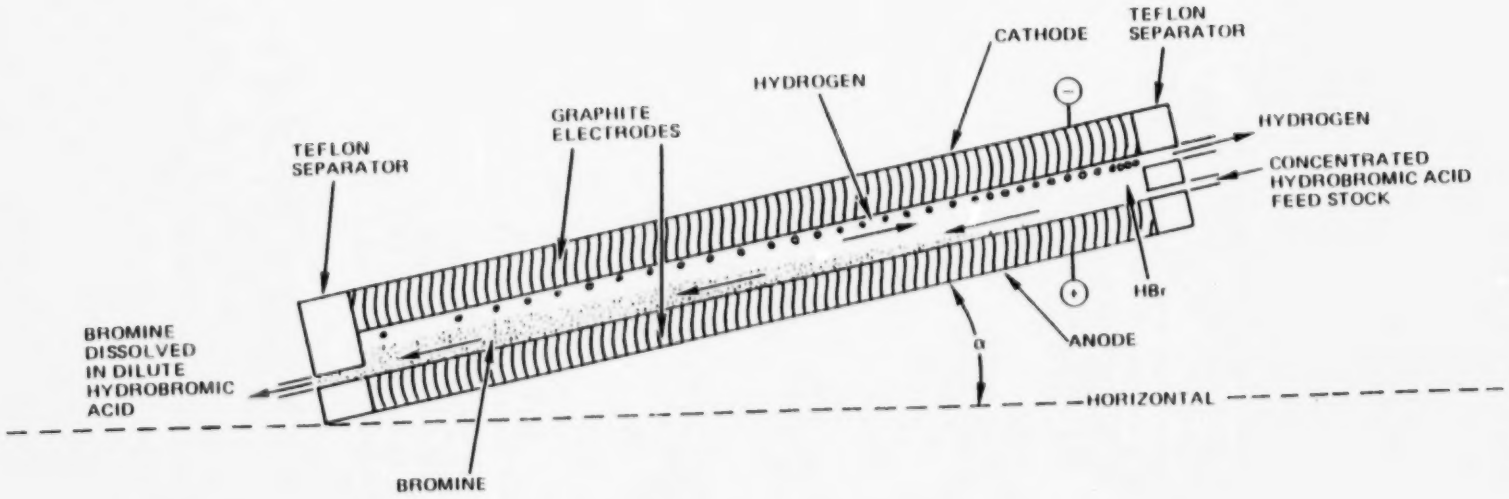

Figure 14. Membraneless Electrolysis Cell

TABLE 6. COULOMBIC EFFICIENCY OF MEMBRANELESS CELL

Electrode Current Density (mA/cm^2)	Electrode Angle (a) (Degrees from Horizontal)	Coulombic Efficiency (Percent)
50	16	66
100	16	64
50	3	96
100	3	92

Decreasing the electrode angle from 16° to 3° resulted in approximately 50% increase in coulombic efficiency. The reason for this is probably that less mixing occurred and, thus, less transport of the more dense bromine (as Br_3^- formed at the bottom electrode) to the cathode (upper electrode) occurred.

Doubling the current density had the effect of slightly decreasing the coulombic efficiency of the cell. This is probably due to an increase in turbulence in the liquid phase, due to the increase in hydrogen generation. Turbulence, in turn, contributes to transport of Br_3^- to the cathode, where the competing electrochemical reaction can occur. Tests also showed that the voltage required for decomposition of a 47 wt % HBr solution at 25°C was similar to the decomposition voltage in the 4-liter membrane-type cell.*

These tests thus indicated that the inclined membraneless cell concept is preferable to the batch-type membrane cell. A bromine regeneration pilot system was then set up around this inclined membraneless cell as shown in Figure 15. A photograph of the apparatus is shown in Figure 16.

Electric power for the pilot-scale regeneration system was supplied by a Hewlett-Packard Model 6455A DC power supply. The cell voltage was measured at probes attached to the graphite electrodes. The voltage readout was with a Keithly Model 160 digital multimeter and dual-channel strip chart recorder. The electrolysis cell current was passed through a shunt and attached to a DC ammeter and then to the other channel of the dual channel strip chart recorder.

A peristaltic pump was used to feed the concentrated HBr solution through the inclined membraneless electrolysis cell. The electrolyte flow rate was controlled by a variable speed electric motor mechanically coupled to the peristaltic pump. The concentrated HBr electrolyte was pumped from an electrolyte reservoir into the elevated port of the electrolysis cell (Figure 14). The electrolyte entered the cell by means of ports or slots at the anode (lower electrode) electrolyte interface. The bromine/dilute HBr electrolyte exited the electrolysis cell at the opposite end of the

* In order to make the tests comparable, electrolysis was carried out on HBr solutions containing less than 0.5 wt % bromine and with the membraneless cell filled with 47 wt % HBr under a static or no-flow condition.

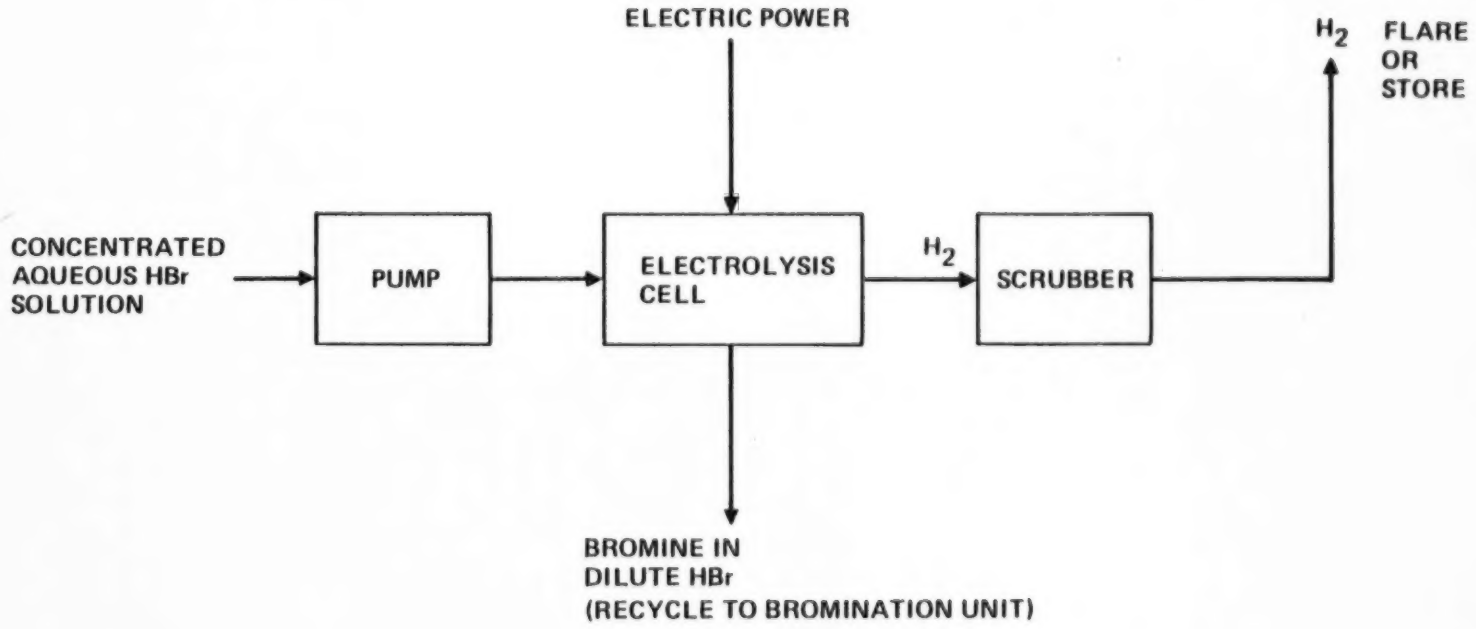

Figure 15. Schematic Diagram of Bromine Regeneration Pilot System

Figure 16. Pilot-Scale Bromine Regeneration System

cell, which was at a lower elevation. The Br_2/dilute HBr solution was collected and stored in a reservoir for subsequent reuse in the bromination reaction.

The hydrogen generated from the electrolysis of aqueous HBr exited the cell at ports on the undersurface of the cathode (upper electrode) at the cell's elevated end (Figure 14). The hydrogen was passed through a gas scrubber system to remove Br_2 and HBr vapors. (The electrolysis cell itself may be considered to act as the first stage of a scrubber for Br_2 since the H_2 flow is countercurrent to the Br_2 (or HBr_3) flow through the cell.) The H_2 gas scrubber system consisted of two scrubbers in series; the first used water to remove HBr vapors, and the second contained a 5 wt % aqueous NaBr solution to remove Br_2 and HBr. The H_2 effluent from the scrubbers was analyzed by a specific ion electrode technique and was found to contain less than 2 ppm (by volume) total Br_2/HBr. Addition of a third scrubber containing 10 wt % NaOH reduced the total Br_2/HBr content to 0.1 ppm by volume (the limit of detection of the analytical method).

Test Results

The bromine regeneration pilot-unit was used to conduct electrolysis tests on an aqueous 38 wt % HBr solution formed by the reaction of a Malathion-debris mixture with bromine and water. This solution also contained approximately 2 moles of H_2SO_4 and 1 mole of H_3PO_4 per 64 moles of HBr.* The tests were conducted at 25°C with the electrodes inclined at 3° from the horizontal position. The HBr electrolyte was passed through the cell at a rate of 2 cc/min. The interelectrode cell volume was 63.5 cc; thus, the electrolyte residence time in the cell was approximately 30 min. The decomposition voltage of this solution was measured as a function of electrode current density from 20 to 200 mA/cm^2. The results are given in Table 7 and are also shown graphically in Figure 17. The decomposition voltages measured using the vertical 4-liter cell with a 0.1-cm-thick fibered felt membrane separator are also shown for comparison in Figure 17. The decomposition voltage vs electrode current density data were similar for the two types of cells; however, the coulombic efficiency of the membraneless flow-type cell was much higher than that of the batch-type cell, employing an Al_2O_3 membrane separator.

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* Chemical analysis of the solutions from the laboratory-scale tests showed that Malathion reacts with bromine and water as follows:

$$C_{10}H_{19}O_6PS_2 + 26\ H_2O + 32\ Br_2 \longrightarrow 10\ CO_2 + 64\ HBr + 2\ H_2SO_4 + H_3PO_4.$$

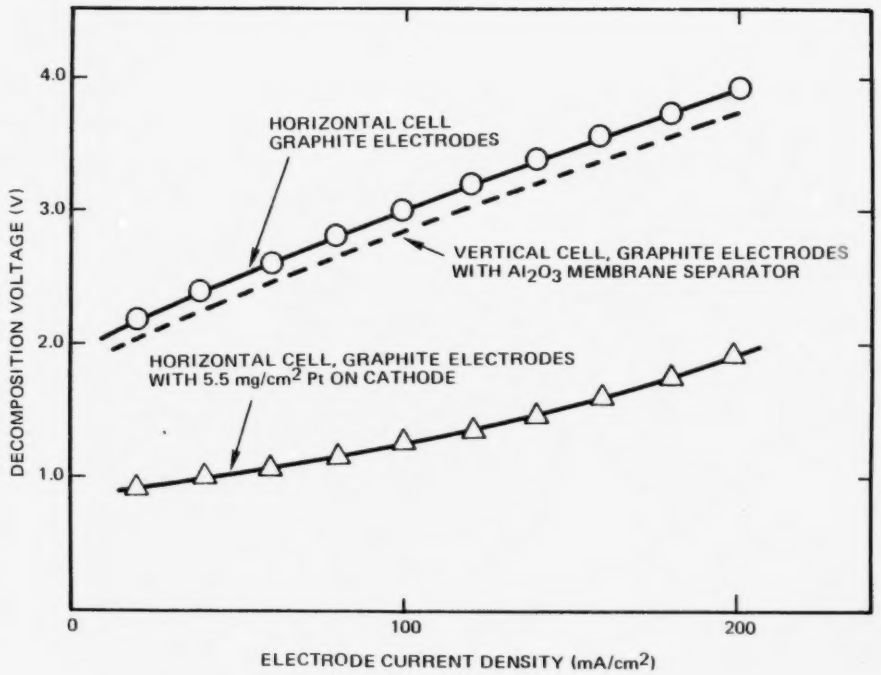

Figure 17. Effect of Membrane Separator and Effect of Platinized Cathode on Decomposition Voltage of a 38 wt % Aqueous HBr Solution at 25°C

TABLE 7. DECOMPOSITION VOLTAGE VS. ELECTRODE CURRENT DENSITY FOR A 38 WT % AQUEOUS HBr SOLUTION AT 25°C USING GRAPHITE ELECTRODES

Current Density (mA/cm^2)	Decomposition Voltage (Volts)	
	Run 1	Run 2
20	2.13	2.13
40	2.30	2.34
60	2.55	2.53
80	2.77	2.77
100	2.93	2.97
120	3.13	3.11
140	3.31	3.30
160	3.54	3.46
180	3.70	3.72
200	3.89	3.91

The inclined membraneless cell is simple in design and operation and gives high coulombic efficiencies. However, the voltage, and thus the energy, required to carry out HBr electrolysis at viable current densities (i.e., 100 to 200 mA/cm^2, comparable to current densities employed in commercial electrolysis processes such as generation of hydrogen and chlorine) is approximately 4 to 5 times greater than the no-load or thermodynamic potential of 0.68 volts measured at 25°C. This high decomposition voltage is attributed to overvoltage at the hydrogen-graphite cathode.[2, 3] To reduce the electrolysis voltage under viable load conditions, tests were conducted with a platinized cathode.

Platinized Graphite Cathode

Electrolysis tests were conducted with HBr solutions from the bromination of the Malathion-debris mixture, using a graphite cathode coated with 5.5 mg/cm^2 of platinum, obtained by electrochemical deposition from a 2 wt % solution of hexachloroplatinic acid. The graphite anode was not platinized (same as in the previous tests). The decomposition voltage of the HBr solution was measured as a function of electrode current density; the results are given in Table 8 and in Figure 17. It is seen that the deposition of 5.5 mg/cm^2 of platinum on the cathode surface reduced the decomposition voltage under load to less than half the value required at comparable current densities with a graphite cathode. Thus, the use of only small amounts of platinum on the graphite cathode reduced the electric power required for electrolytic regeneration of the bromine by about one-half.

The bromine regeneration pilot-scale system was operated continuously for 4 hr (using the 38 wt % HBr aqueous solution made in the bromination reaction pilot-scale tests) at a current density of 100 mA/cm^2, without any detectable deterioration of the platinized cathode, i.e., the decomposition voltage remained constant at 1.25 $\pm$ 0.05 V for the duration

TABLE 8. DECOMPOSITION VOLTAGE VS. ELECTRODE CURRENT DENSITY FOR A 38 WT % AQUEOUS HBr SOLUTION AT 25°C USING A PLATINIZED GRAPHITE CATHODE

Current Density (mA/cm^2)	Decomposition Voltage (Volts)	
	Run 1	Run 2
20	0.91	0.89
40	1.05	1.05
60	1.13	1.15
80	1.18	1.22
100	1.25	1.24
120	1.40	1.38
140	1.47	1.49
160	1.58	1.60
180	1.74	1.78
200	1.94	1.90

of this test. The electrolyte flow rate through the cell was maintained at 2.2 cc/min. After steady-state concentrations had been attained, the effluent from the cell contained 22 wt % HBr with 16 wt % dissolved bromine as a single liquid phase. The coulombic efficiency of the electrolysis cell during this test was determined by measuring the amount of hydrogen formed and comparing this with the amount expected from the current passed through the cell. Coulombic efficiencies of about 96 $\pm$ 1% were obtained at electrode current densities from 50 to 200 mA/cm^2.

These tests demonstrated that the inclined membraneless electrolysis cell can be used to regenerate the bromine at a viable current density of 100 to 200 mA/cm^2 at 96 $\pm$ 1% coulombic efficiency. Furthermore, this can be achieved with a single pass of the electrolyte through the electrolysis cell. For example, using a typical aqueous solution feed stock from the bromination step containing 38 wt % aqueous HBr, electrolysis can be performed in this cell to obtain an effluent containing 22 wt % HBr and 16 wt % dissolved Br_2, which is suitable for recycle to the bromination step of the process.

Engineering Study

Design Concept

Survey of the literature [5] and discussions with Dr. Basil Mercer of Battelle-Northwest (January 1979) suggested that a unit with a capacity of about 22.7 kg (50 lb) of hazardous chemical would be appropriate for disposal of spilled hazardous chemicals. This preference was based on the magnitude of most frequently reported hazardous chemical spills. In the interest of minimizing capital expenditures, the decision was made to use an operational mode in which the bromination reactor is operated batch-wise and the bromine regeneration unit is operated continuously.

Assumptions

The laboratory and pilot-scale studies showed that destruction of the hazardous chemical was complete in 2 hr or less at 300°C. A 2 hr reaction time, at 300°C and 8500 kPa (1200 psi), was therefore assumed for the bromination unit with a 1 hr turnaround. The rest of the system operates continuously at ambient temperature and pressure. Thus, the equivalent processing rate is 7.5 kg/hr (16.7 lb/hr) of hazardous chemical. The following assumptions were also made to compute the material balance and to establish the size of the components:

1) The hazardous chemical for disposal is mixed with debris consisting of 10 wt % sand, 10 wt % soil, 5 wt % humus, and 5 wt % moisture.

2) Malathion, the selected reference material, reacts completely with Br_2 according to:

$$C_{10}H_{19}O_6PS_2 + 26\ H_2O + 32\ Br_2 \longrightarrow 10\ CO_2 + 64\ HBr + 2\ H_2SO_4 + H_3PO_4.$$

3) Bromine reacts with sand, soil, and humus in quantities of 0.00026, 0.00069 and 0.0296 g-moles/g, respectively (Table 3).

4) The liquid effluent from the bromination reactor consists of the azeotrope (38 wt % HBr at 300°C), solids residues, and mineral acids.

5) Solids capture at the filter section is complete.

6) Ten percent of the feed to the electrolytic cell is sent to the evaporator and lime treatment sections.

7) Gypsum ($CaSO_4$) and calcium phosphate ($Ca_3(PO_4)_2$) are precipitated by lime from the evaporator bottoms product.

8) Water leaching of the solids in the pressure filters displaces all soluble bromides.

9) Equilibrium at 25°C is reached in the cell offgas scrubber with respect to HBr, Br_2, and H_2O.

10) The electrolysis cell operates at 25°C and atmospheric pressure.

11) The electrolysis cell liquid effluent contains 22 wt % aqueous HBr with 16 wt % dissolved Br_2.

Process Description

Figure 18 shows a block diagram of the conceptual disposal system. The

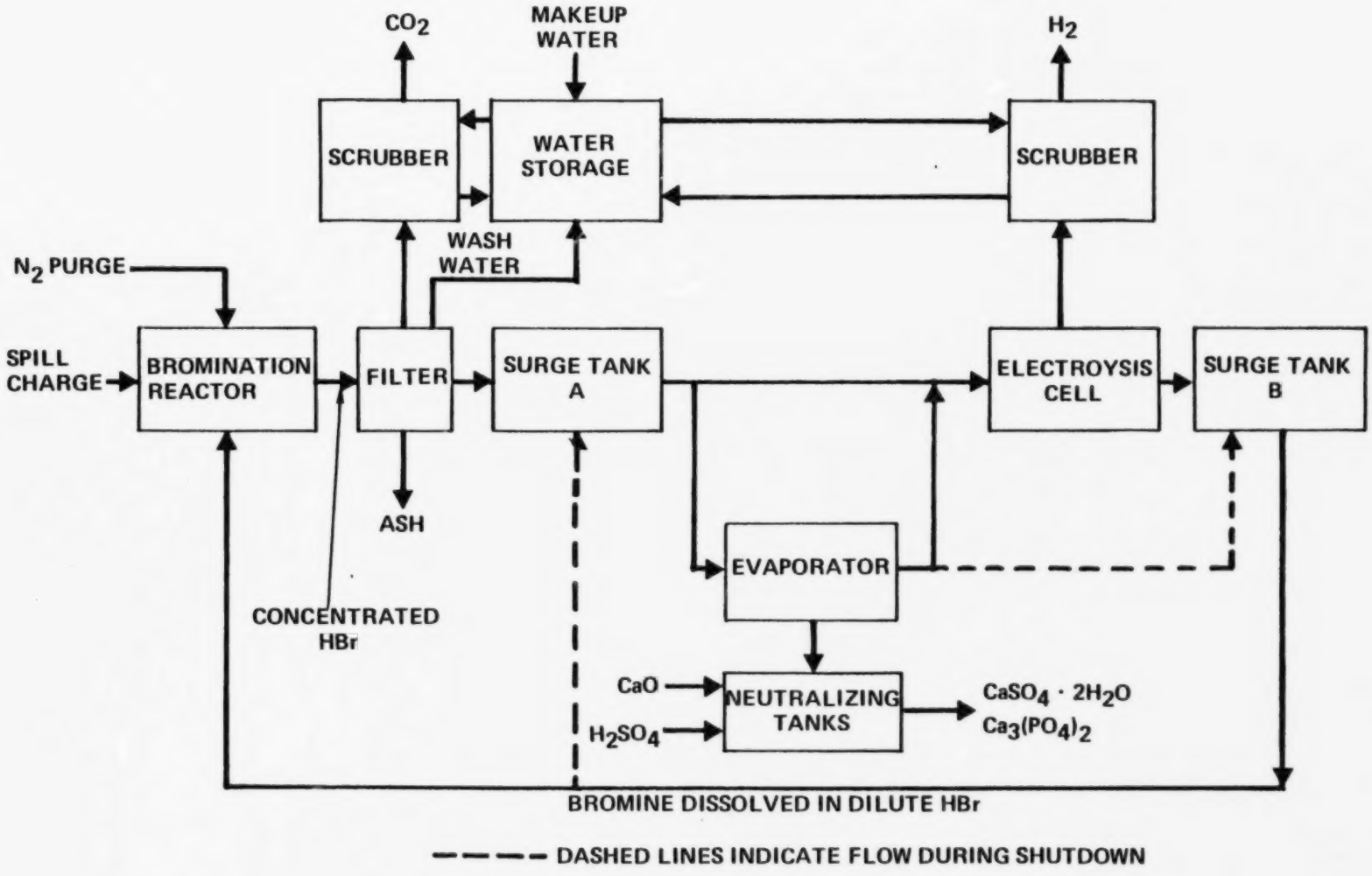

Figure 18. Block Diagram of a Conceptual Disposal System

reference case feed stock selected for this study consists of 70 wt % Malathion mixed with 30 wt % debris consisting of 10 wt % sand, 10 wt % soil, 5 wt % humus, and 5 wt % moisture. This feedstock is fed into the bromination reactor along with the required water and bromine. The latter is in solution as HBr_3 in a recycle stream. A 22.7 kg charge will include 15.9 kg of Malathion and 6.8 kg of debris. This charge is reacted with 32.3 kg of water and 352 kg of Br_2. In addition, 862 kg of water and 243 kg of excess HBr are present to provide the desired azeotrope at the completion of the reaction.

After completion of the bromination reaction (2 hr), the reactor is partially cooled. The residual pressure is used to move the aqueous slurry produced through a bank of pressure leaf filters to remove insoluble residues such as debris. After removal of liquid from the reactor, the residual gases are purged through the filter and then through a packed scrubber. Scrubber offgases consist essentially of CO_2 and N_2 with the equilibrium vapor pressure content of H_2O. The scrub water, with absorbed HBr, is returned to a water storage tank. Water from the storage tank (actually, very dilute HBr solution) is used as makeup water at the reactor and also at the evaporator section (described below), preventing excessive buildup of HBr. Fresh water is used to wash the filter cake to remove entrained bromides from the debris residues and is sent to the water storage tank. Although the wash water entry point is shown at the filter, it is advantageous to add part of the water through the bromination reactor, itself, during the cleanout cycle.

The liquid product (38 wt % azeotropic mixture) from the reactor is allowed to accumulate in Surge Tank A for 2 or 3 cycles at the start of a disposal run, and is used as feedstock for the electrolytic cell, which is then started up and operated continuously. The electrolysis cell operates at atmospheric pressure and at ambient temperature. The 38 wt % HBr is electrolyzed to produce H_2 gas and Br_2, which remains in solution. The liquid effluent is nominally a 22 wt % aqueous HBr solution with about 16 wt % dissolved Br_2 (as Br_3^-).

A sidestream (10%) of the flow from Tank A to the electrolytic cell is diverted to an evaporator section to concentrate the soluble mineral bromides, sulfuric and phosphoric acids produced in the bromination reactor. Operating at atmospheric pressure, the evaporator, which is a jacketed, glass-lined vessel equipped with a reflux column, distills off the $HBr-H_2O$ solution. The overhead product flows to the electrolysis cell feed. The bottom liquor, containing mineral bromides as well as concentrated phosphoric and sulfuric acids, is discharged through neutralizing tanks in which sulfate and phosphate are precipitated with lime as gypsum and calcium phosphate. Excess lime is neutralized, as required, with H_2SO_4. Most of the metallic ions are precipitated by the excess lime in the first neutralizing vessel. Water lost with the gypsum/phosphate sludge (some of the water loss is hydrate water and some is entrained) is made up from the water supply tank to return the electrolytic cell feed to the azeotropic concentration. The liquid effluent from the electrolytic cell (16 wt % Br_2 in 22 wt % HBr aqueous solution) is sent to Surge Tank B, from which intermittent charges for the batch reactor are withdrawn. The gaseous

product, H_2, from the electrolysis cell, is scrubbed in a reflux column using water from the water storage tank.

When a disposal run is terminated, all the liquour in Tank A is sent through the evaporator/acid concentrator to remove all mineral acids and mineral bromides. The concentrated 38 wt % HBr aqueous solution is temporarily stored in Tank B and then returned for storage to Tank A to complete the cycle (dotted lines in Figure 18).

Capital Cost

Estimates were made of the cost of the major pieces of equipment using cost data published in References 6-9. Vendor price quotes were used to develop a price basis for tantalum-lined pressure vessels from which the cost of the 22.7 kg batch reactor was estimated. It was estimated that a vessel with a volume of about 800 liters will be required for this unit. The cost of the electrolytic cell was estimated, in part, from data given in Reference 3. All costs were adjusted, using appropriate economic indicators, to January 1979. Table 9 lists the major pieces of equipment for which cost estimates were obtained.

The cost of the electrolytic cell was estimated in 1977 to be about $\$550/m^2$ (Reference 3). The cited paper compared this to a water electrolyzer which, it stated, ran about $\$750/m^2$. In Reference 9, however, the cost of a water electrolyzer was placed at as much as $\$1000/m^2$ in 1975. Using this figure and the relative costs of Reference 3, the cost for an HBr electrolyzer was estimated and updated to 1979 dollars at $\$1000/m^2$. About 20 m^2 are required for the present process.

The estimated equipment costs for the 22.7 kg batch-size hazardous chemical disposal system are given in Table 8. The reference(s) used to arrive at the cost of each item are also shown.

Installation, piping, construction, and overhead costs were developed from the major equipment costs using the methods presented by Lang.[6,7,8] An additional $50,000 was added for minor equipment (e.g., filters, pumps, instrumentation, tank cooling coils, etc., but not utility services, valves, etc.). Table 10 summarizes the cost for the 22.7 kg disposal system.

In summary, conceptual engineering studies were carried out on a system for disposal of spilled hazardous chemicals. A bromination reactor operating batch-wise, with a capacity of about 22.7 kg (50 lb) of hazardous chemicals,was assumed. Operation was assumed at 300°C and 8500 kPa (1200 psi) with a turnaround time of 1 hr for an average processing rate of 7.5 kg/hr of hazardous chemical. The aqueous HBr solution from the bromination reactor is stored and then sent to a continuously operated electrolysis cell for regeneration of the bromine. The electrolysis cell was assumed to operate at ambient temperature and pressure at an electrode current density of 100 mA/cm^2. Preliminary estimates indicate that the cost of equipment for such a disposal system would be about $350,000. The estimated total capital cost,including the installation at an available site,is $625,000.

TABLE 9. EQUIPMENT COST BREAKDOWN

Item	Description	Cost *	Reference
1	Tank, pressure, carbon steel, tantalum lined, 8500 kPa working pressure, 300°C, 800 liters, semielliptical heads, L/D = 3.8	$200,000	**
2	Cell, electrolytic, graphite construction, diaphragm-free, 20 m^2 electrode area	20,000	3, 9
3	Evaporator, glass-lined vessel, 200 liters, steam jacketed, with glass-lined reflux column and condenser	25,200	10
4	Two tanks, neutralizing, 800 liters, glass-lined, closed	10,600	10, 11
5	Two scrubber columns, packed, glass-lined, 10 cm ID, 3 m length	8,000	10
6	Two tanks, storage, HBr-H_2O-Br_2 solutions, 7200 liters	20,000	11
7	Boiler, steam, 64 kg/hr at 160°C	7,500	12
8	Tank, water storage (dilute HBr) glass-lined, 6000 liters	8,500	13
	Total Major Equipment Cost	$299,800	

* Cost figures adjusted to January 1979.

** D. Moore, Fansteel, Special Structures Division, Torrance, California, private communication February 1979.

TABLE 10. COST SUMMARY FOR A 22.7 KG BATCH-SIZE HAZARDOUS CHEMICAL DISPOSAL SYSTEM

Item	Cost *
Major equipment listed in Table 9	$299,800
Minor equipment	50,000
Total Equipment	$349,800
Installation cost: Includes material and labor to install, including foundations, supports, chutes, vents, insulation, etc. (43% total equipment cost)	$150,000
Installed Cost	$499,800
Piping costs (25% of installed equipment cost)	$125,000
Installed cost with piping on an available site	$624,800

* Cost figures adjusted to January 1979.

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